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Triggered Formation of Thixotropic Hydrogels by Balancing Competitive Supramolecular Synthons†

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Two component hydrogels have been obtained by formation of 1:1 complexes of bis(pyridyl urea)s with a range of dicarboxylic acids. The gels are thixotropic and undergo an assembly process in which short segments can reversibly assemble into an interconnected fibrous network. NMR and IR spectroscopic data suggest that the gelators form neutral gelator-acid complexes rather than salts. The use of dicarboxylic acids to trigger gelation in bis(pyridyl urea)s parallels analogous triggered gelation of metal ions and halogen bond donors in related systems.

Introduction

Gels derived from low molecular weight gelators (LMWG) have experienced an explosion of interest in recent years.[1-13] Gels, particularly hydrogels[14] where water is the fluid phase, are everyday materials with applications in drug delivery,[15, 16] wound healing,[17] templating both inorganic and organic nanostructures, such as metallic nanoparticles and porous polymers,[18-22] and in crystal growth.[23, 24] LMWG aggregate into cross-linked fibres *via* non-covalent interactions such as hydrogen bonding and, in water particularly, hydrophobic effects.[14] The growing interest in their properties stems from their generally facile synthesis, their synthetic and structural versatility, and the possibility of adaptive or reversible gelation offered by the weak, dynamic supramolecular interactions holding the fibres together.[7] The mechanism of the non-equilibrium self-assembly process involved in gel formation by LMWG is also fascinating from a fundamental viewpoint and is perhaps a more tractable problem in well-defined small molecules than in more conventional silica or biopolymer based hydrogels. Of particular current interest are multicomponent gels.[25] These systems may comprise stoichiometric co-gels in which two non-gelator components combine in a well-defined way to produce a gel-forming supermolecule, or they may be blends of LMWG (sometimes termed 'multi-gelator gels') that are individually gelators.[26-32] Some metallogels arising from metal cross-linking of gelating ligands,[4, 6, 33] or anion influenced gels also fall into the broad category of multicomponent gels.[34-36] In previous work we have looked at triggered gelation in 'inhibited gelators', particularly pyridyl ureas.[37, 38] Intramolecular CH···O interactions coupled with the good hydrogen bond acceptor ability of the pyridyl nitrogen atom make pyridyl ureas particularly poor gelators (Fig. 1b)[37, 39-41] because they cannot effectively form the typical urea α-tape motif generally thought to be responsible for one-dimensional fibre growth and hence gel formation (Fig. 1a).[42, 43] Addition of a co-gelator such as a metal ion[38, 44-46] or halogen bond donor[47] results in coordination to the pyridyl nitrogen atom hence freeing the urea functionality and switching the system from the urea-pyridyl hydrogen bonding motif to the gel-forming urea α-tape.

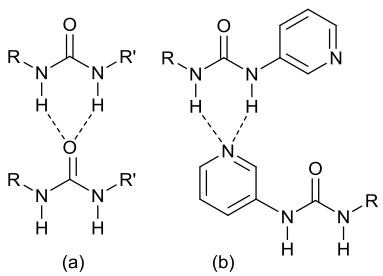


Fig. 1 (a) urea α-tape motif commonly responsible for gel formation, (b) inhibiting urea-pyridyl interaction in pyridyl ureas, making them relatively poor gelators. R = R' = alkyl, aryl *etc.*

Related work by the Dastidar group has shown that co-gels comprising the simple *N,N'*-di-(*n*-pyridyl) urea (*n* = 3 or 4) in conjunction with carboxylic acids also produces a range of composite materials, some of which form gels and others of which are crystalline.[48] This builds on earlier reports of the effective hydrogelation ability of single component gelators containing both urea and carboxylic acid functionality.[49] The Dastidar group characterised a range of materials by single crystal X-ray diffraction which revealed a variety of supramolecular synthons of the types shown in Fig. 2a-c with most exhibiting proton transfer, although some carboxylate functionalities remain protonated. The urea tape motif shown in Fig. 2d is a possibility but was not observed in the experimental structures, and it was proposed that "micropore" formation (Fig. 2c) could be responsible for gelation behaviour in some instances.[48] Interestingly, *N,N'*-di-(4-pyridyl) urea is a hydrogelator in its own right, whereas the *meta* isomer *N,N'*-di-(3-pyridyl) urea is not, possibly because of formation of the synthon shown in Fig 1b. However, in conjunction with four out of eight dicarboxylic acids studied (namely oxalic, succinic,

maleic and L-tartaric acids) this compound forms multi-components gels.[48] We reasoned that hydrogen bonding to the pyridyl nitrogen atom or its protonation could facilitate urea tape formation and hence result in gel formation. While no urea α-tape motifs were observed in the interesting range of X-ray crystal structures reported by the Dastidar group,[48] it is possible that the crystalline structures are not fully representative of the gel phase material.[50] Alternatively gelation by anion-mediated hydrogen bonded tape formation may be involved.[51] In this report we examine multi-component gel formation with extended bis(3-pyridyl urea)s. As single components these pyridyl ureas are poor gelators or non-gelators and hence co-gel formation with carboxylic acids offers the possibility of 'turn-on' gelation and other complex, emergent properties.

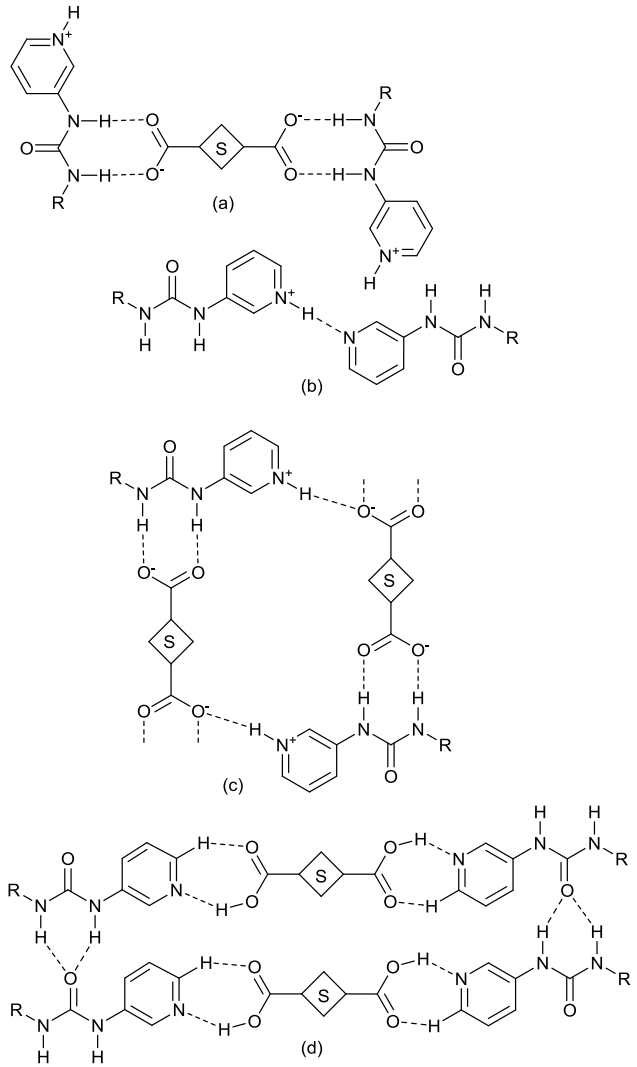
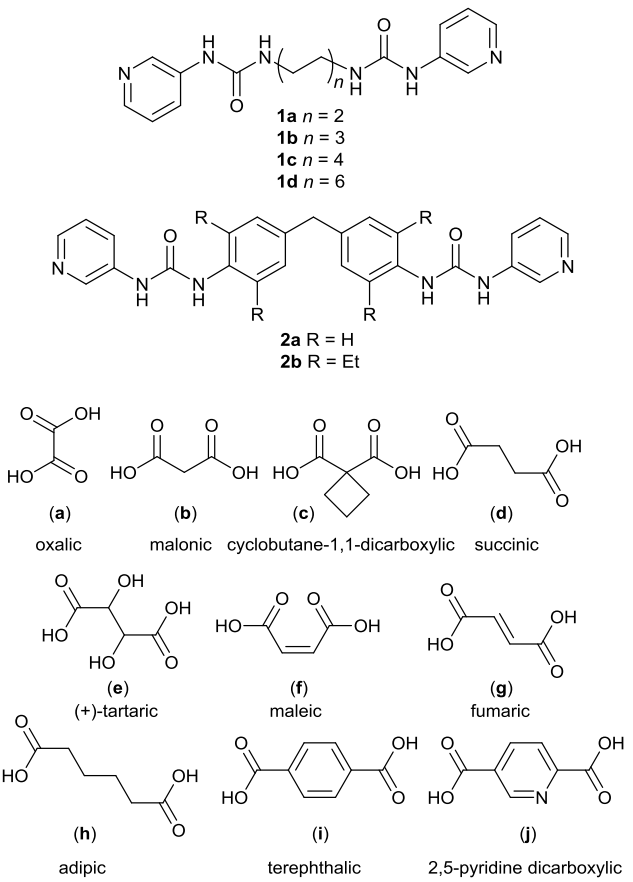


Fig. 2 Supramolecular synthons arising from protonation of a pyridyl urea by dicarboxylic acids (neutral co-crystals of similar structure may also form in the absence of proton transfer in some cases; S = spacer group) (a) $R_2^2(8)$ hydrogen bonded ring, (b) hydrogen bonding of a pyridinium moiety with a neutral pyridyl group (c) composite pattern observed in the structure of *N,N'*-di-(4-pyridyl) urea / adipic acid salt hydrate, for example,[48] (d) urea α-tape formation in conjunction with pyridine-carboxylic acid $R_2^1(7)$ ring formation.

Results and Discussion

The gelation behaviour of two types of bis(3-pyridyl urea) based on either an aliphatic alkylene spacer (**1**)[37] or diphenyl methane spacer (**2**)[52] were examined in conjunction with a range of dicarboxylic acids **a** – **j** in water and polar organic solvents (methanol, ethanol, DMF, DMSO, *c.f.* Table S1-S7 in the Supporting Material). Compounds of type **1** are non-gelators as single components while compounds **2** are weak organogelators (compound **2b** more so than **2a**).[52] None of the pyridyl ureas studied act as hydrogelators, an observation correlated with the competition from urea-pyridyl hydrogen bonding evident in the X-ray structures of this class of compound.[37, 39] Gelation experiments were undertaken in three different ways for each sample by either by either shaking the components in solvent at room temperature, sonication or warming and cooling the bis(urea)/dicarboxylic acid mixtures in solvent at 1% weight/volume (w/v). Using all three methods, the short-chain compounds **1a–c** formed precipitates in water in the presence of a stoichiometric amount of all dicarboxylic acids **a**–**j** and did not exhibit any gelation behaviour. Mixtures of the dicarboxylic acids with the longer homologue **1d** also gave precipitates and did not result in gel formation, however turbid solutions were observed in the presence of malonic, (+)-tartaric and 2,5-pyridine dicarboxylic acids (**a**, **e** and **j**).



In contrast to compounds of type **1**, binary mixtures of compounds **2** with various dicarboxylic gave very interesting two-component hydrogelation properties, with carboxylic acid adducts of **2a** in particular proving highly effective. Stoichiometric mixtures of **2a** with oxalic (**a**), tartaric (**e**) maleic

(**f**) and 2,5-pyridine dicarboxylic (**j**) acids gave rise of hydrogels simply by manual agitation at room temperature. Viscous solutions were also observed for cyclobutane-1,1-dicarboxylic acid (**c**) and terephthalic acid (**i**). The more hydrophobic ligand **2b** formed hydrogels in the presence of tartaric acid (**e**) and weak gels or viscous solutions in the presence of malonic (**b**), adipic (**h**) and 2,5-pyridine dicarboxylic (**j**) acids.

The hydrogels of **2a** with acids **a**, **e** and **j** all proved to be thixotropic,[53-56] collapsing to sols upon shaking or sonication at room temperature before regaining their gel character on standing over a period of around 30 min. The gels are not thermoreversible and form precipitates upon warming and cooling. The **2a**·oxalic acid and 2,5-pyridine dicarboxylic acid gels are the most mechanically stable and have a critical gelation concentration (CGC) of 0.4 % w/v (total gelator *vs.* solvent), with other gels exhibiting a CGC close to 1% w/v. Stress and frequency sweep rheometry demonstrated that the gel strength as measured by the elastic modulus decreases in the sequence 2,5-pyridine dicarboxylic > oxalic > tartaric > maleic acids. The fact that *G*' is around one order of magnitude greater than *G*" for all samples confirms the solid-like gel phase nature of the materials, Fig. 3.[6] The elastic modulus also proved invariant with sweep frequency.

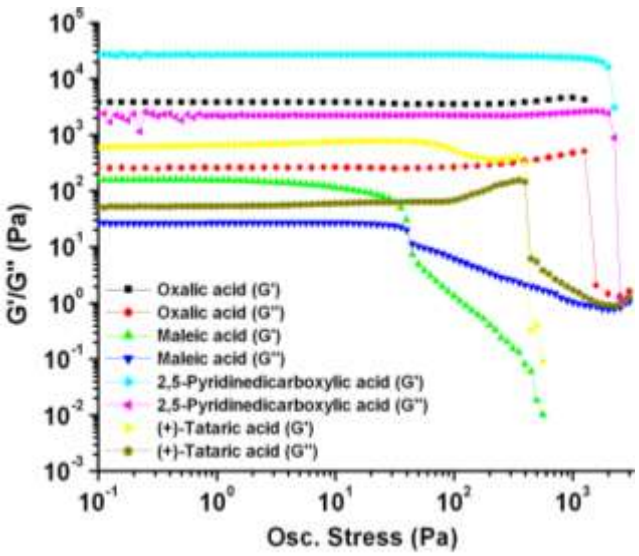


Fig. 3 Stress sweeps of hydrogels of **2a** with oxalic acid, maleic acid, 2, 5-pyridinecarboxylic acid and (+)-tartaric acid (1:1 ratio, 2.0 w/v%)

Combination of varying ratios of **2a**:acid from 3:1 to 1:3 demonstrated that the most stable gels form at a 1:1 stoichiometry, consistent with matching the dicarboxylic acid to the two basic pyridyl functionalities. Optimal gelation at a 1:1 ratio was confirmed by stress and frequency sweep rheometry (see supplementary information, Fig. S1 and S2). Gels of 2,5-pyridine dicarboxylic acid proved more tolerant of excess acid than the other systems, correlating with the additional pyridyl group on the acid. Addition of triethylamine to gels of **2a** resulted in their collapse to a sol, however the gel could be re-generated by addition of more dicarboxylic acid suggesting a requirement for relatively acidic pH and hence perhaps protonation of the pyridyl groups. The gelation behaviour is summarised in Fig. 4.

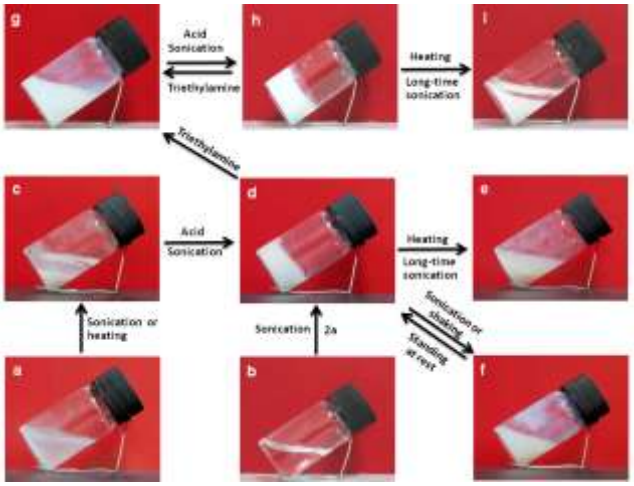


Fig. 4 (a) mixture of **2a** and water; (b) dicarboxylic acid solution; (c) insoluble **2a** following sonication or heating; (d) **2a**·oxalic acid gel; (e) phase separation on heating/cooling or extended sonication; (f and g) sol state after sonication or addition of triethylamine; (h) **2a**·oxalic acid gel following treatment with triethylamine and then further oxalic acid; (i) precipitate following heating/cooling or sonication.

The gelation of the **2a**/acid systems at room temperature and their thixotropic behaviour were probed by a range of rheological experiments. Time sweep rheometry clearly demonstrates the gelation of a 1:1 mixture of **2a**·oxalic acid with an elastic modulus (*G*') of *ca.* 10^3 Pa achieved approximately one hour after disrupting the gel by shaking a 1% w/v mixture, Fig. 5. Five repeated cycles of shaking and re-formation showed that the samples reproducibly regain their mechanical properties after disruption without any degradation within experimental error (supplementary material, Fig. S5).

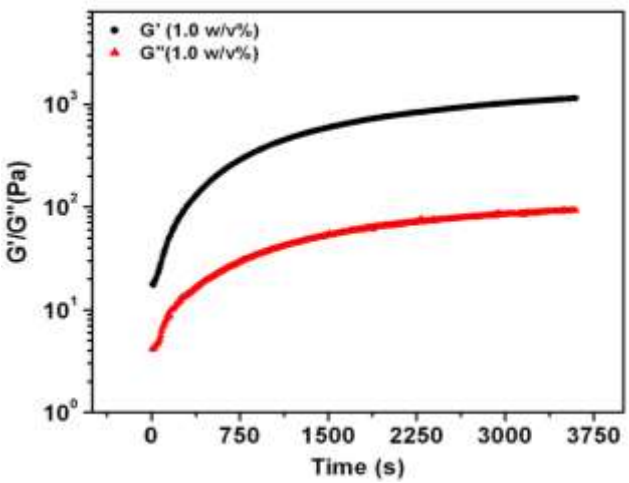


Fig. 5 time sweep rheology for the thixotropic 1:1 mixture of **2a**·oxalic acid (1% w/v) following disruption by mechanical agitation.

The morphology of the freeze-dried gels was examined by SEM (see experimental section), which revealed a homogeneous fibrous network, Fig. 6a. At low concentration (0.5 % w/v) the fibres proved to be relatively thin with average diameter 25 – 40 nm. As concentration increased to 3 % w/v some bundling of the fibres was observed. The morphology of the **2a** acid gels proved similar for all acids studied (see supplementary material, Fig. S6

and S7).

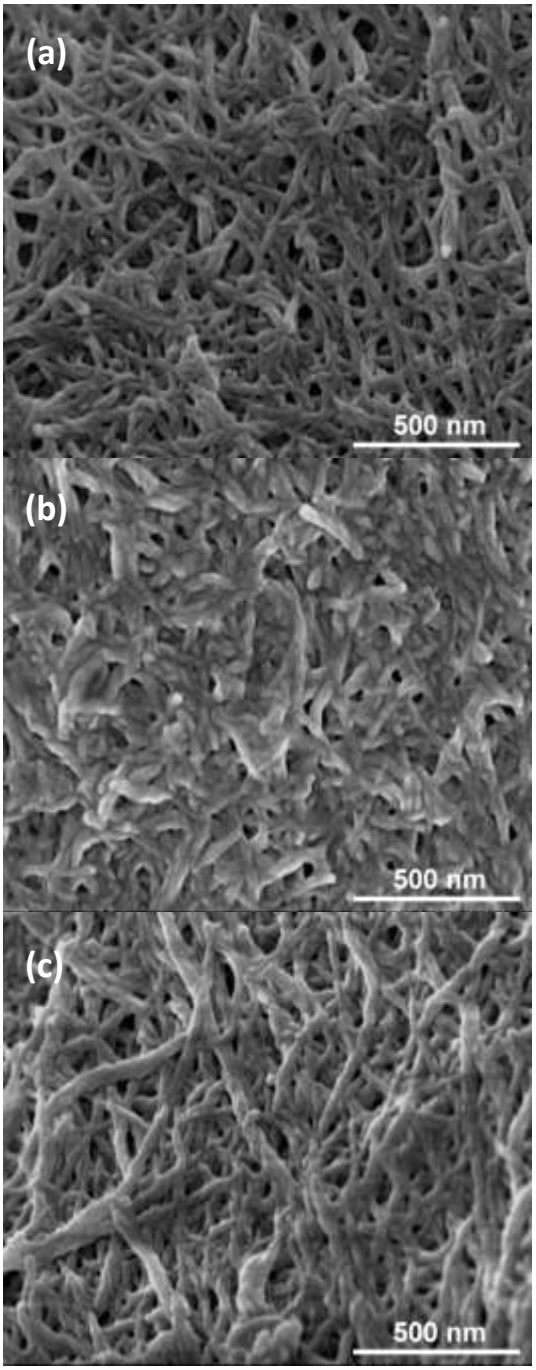


Fig. 6 SEM images of freeze-dried gels of **2a**·oxalic acid (1:1, 0.5 % w/v) (a) as prepared showing the homogeneous fibrous structure, (b) after degradation by sonication, (c) "recovered" gel sample after standing following sonication.

Upon shaking or extended ultrasonication the gels degrade into sols and begin to flow. Examination of a sonicated sample by SEM (Fig. 6b) shows the presence of some shorter, less interconnected fibres. Upon prolonged standing the gel re-forms and SEM indicates that the interconnected network of longer fibres is re-established (Fig. 6c). This kind of propensity to break down into smaller fragments is characteristic of thixotropic behaviour and offers an explanation of the shear thinning response of the material.[54, 56-58] Mechanical agitation results in break-down of the fibres into individual short lengths of fibre and hence loss of network stability. On standing the fibres reassemble into a sample-spanning network.

The question arises as to whether the two component hydrogels obtained arise from protonation of bis(ureas) of type **2** by the dicarboxylic acids or whether they are neutral co-gels. Consideration of the pK_a values of oxalic acid of 1.25 and 3.81[59] compared to the pyridinium ion of 5.23[59] suggests that oxalic acid may well protonate pyridine derivatives in aqueous solution. However the IR spectrum of the solid **2a**·oxalic acid xerogel reveals a prominent peak at 1710 cm^{-1} assigned to –COOH.[60] ^{1}H NMR spectroscopic titration of **2a** with oxalic acid in DMSO-d_6 solution (D_2O was avoided to avoid exchange of the NH protons for deuterium and because of the gel formation in that solvent) revealed a consistent downfield shift in the NH resonances on addition of up to three molar equivalents of oxalic acid with the maximum $\Delta\delta$ around 0.8 ppm, consistent with increasing hydrogen bonding to both protons. Modest downfield shifts were also observed for the pyridyl CH resonances. However, the changes are far less pronounced that observed on analogous titration with deuterated hydrochloric acid (DCl) even though the chloride anion is a poorer hydrogen bond acceptor than carboxylates and generally gives lower $\Delta\delta$ values. In addition no clear resonance was observed assignable to a pyridinium NH proton, just a gradually shifting, broad feature moving from 3.3 to 5.3 ppm during the titration assigned to hydrated acidic protons (see supplementary material, Fig. S8 and S11). Similarly the $^{13}C\{^1H\}$ NMR spectrum of a 1:1 **2a**·oxalic acid mixture much more closely resembles the free bis(urea) than the DCl salt. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2a** on addition of 2,5-pyridine dicarboxylic and tartaric acids showed very little change, with the maximum $\Delta\delta$ for the NH resonances of less than 0.2 ppm in each case despite the fact that 2,5-pyridine dicarboxylic acid results in the strongest gels. This lack of response is despite the fact that these compounds are also stronger acids than the pyridinium ion; pK_a values for 2,5-pyridine dicarboxylic acid are 2.35 and 4.96[61] and for (+)-tartaric acid are 2.98 and 4.34.[59] The IR spectra of the **2a** xerogels with 2,5-pyridine dicarboxylic acid and (+)-tartaric acid showed bands at 1710 and 1702 cm^{-1}, respectively assignable to protonated –COOH.[60] Overall the evidence therefore suggests some modest degree of proton transfer in DMSO solution by oxalic acid but very little in the case of 2,5-pyridine dicarboxylic and tartaric acids. The solid xerogels also appear to be neutral co-gel type substances rather than salts. In the work on analogous di-*n*-pyridyl urea carboxylic acid complexes by the Dastidar group, IR and crystallographic data indicated salt formation in the majority of cases, although not all.[48] These di-*n*-pyridyl ureas are likely to be somewhat more basic than compound **2a** and the urea carbonyl group a poorer hydrogen bond acceptor because of intramolecular CH···O interactions, disfavouring urea tape hydrogen bonding and promoting urea carboxylate interactions.[40] However, the factors affecting salt *vs.* neutral co-complex formation in these systems appear to be finely poised.

Variable temperature ^{1}H NMR titration of **2a** in the presence of one molar equivalent of carboxylic acid from 25 to 80^{o}C in DMSO-d_6 showed a consistent up field shift in the urea NH

resonances (**a1** and **a2**) that is reversible on cooling, Figure 7. The other resonances are very little affected. This suggests decreased hydrogen bonding and hence deaggregation on warming, consistent with the behaviour of many urea tape hydrogen bonded systems.[62] The chemical shift change with temperature is almost identical for the oxalic, 2,5-pyridine dicarboxylic and tartaric acid samples and the magnitude of the shift is significantly greater than the change observed on titration with the acid. This data indicates urea tape type hydrogen bonding and urea self-association, at least in DMSO solution.

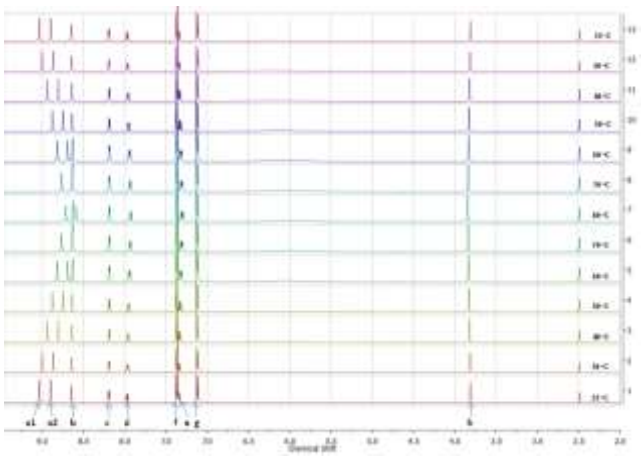


Fig. 7 Variable temperature ^{1}H NMR spectra of a 1:1 mixture of **2a** and oxalic acid. The NH resonances are labelled **a1** and **a2**.

Conclusions

Dicarboxylic acids form neutral complexes with bis(pyridyl urea) gelators of type **2**. The lack of proton transfer suggests that a carboxylic acid – pyridyl interaction accompanied by the urea α-tape motif (Fig. 2d) is a possible structural model for the assembly. This hypothesis is not consistent with the X-ray crystal structures observed by Dastidar and co-workers for dipyridylureas[48] but the neutral acid-pyridyl synthon is well precedented in a range of acid-pyridine derivatives in the CSD. For example the Nangia group have structurally characterised a neutral dicarboxylic acid dipyridyl urea co-crystal of di-3-pyridyl urea and succinic acid (Figure 8a)[40] containing a combination of neutral acid $R_2^2(7)$ pyridyl synthon and urea···acid hydrogen bonding, which might also form in the present systems. However the urea carbonyl group in dipyridyl ureas is a much poorer hydrogen bond acceptor than in aryl ureas related to **2** which can rotate the aryl group out of the urea plane and for a urea α-tape motif, as in the dihydrate of 3-pyridyl-4-tolyl urea (Figure 8b).[37] Ureas of type **1** also interact with dicarboxylic acids but the resulting species are insoluble and do not form gels. Gelation in 1:1 complexes of type **2**·dicarboxylic acid proceeds by a two-step assembly mechanism in which short fibres reversibly assemble into extended fibrous networks. This process seems to be the root cause of the gels' thixotropy and lack of thermoreversibility and highlights the role of kinetic factors, particular growth *versus* precipitation rates in the formation of organic microstructured materials of this type. In order to achieve gelation uniaxial growth is a key requirement. The present data does not unambiguously differentiate between direct urea-urea interactions or carboxylic acid bridged urea-urea interactions. However, the ability of dicarboxylic acids to trigger gelation in bis(pyridyl urea)s of type **2** is clear and, by analogy with metal ion[38] and halogen bond donor[47] triggered gelation, likely has its origins in the interruption of the inhibitory urea-pyridyl interaction shown in Figure 1b.

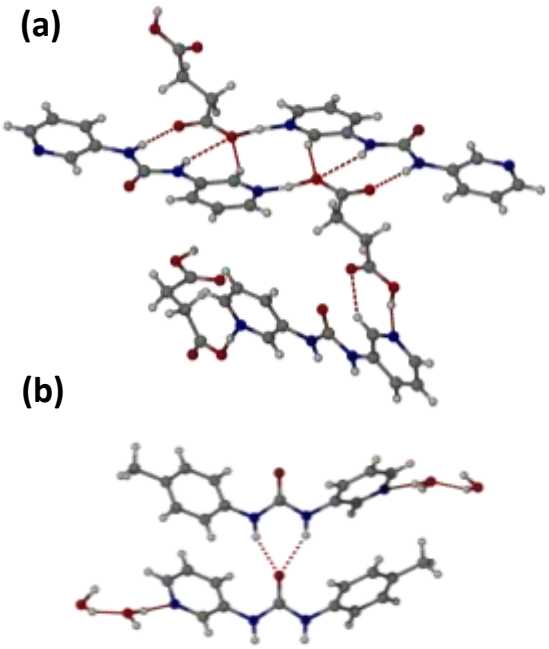


Fig. 8 (a) X-ray crystal structure of the neutral co-crystal of di-3-pyridyl urea and succinic acid[40] showing acid-pyridyl and urea acid hydrogen bonding motifs; (b) X-ray structure of the dihydrate of 3-pyridyl-4-tolyl urea showing the rotation of the aryl group out of the plane of the urea functionality to give a urea a-tape hydrogen bonding motif.[37]

Experimental

Ligands of type **1** and **2** were prepared as described previously.[37, 52] Gelators were screened for gelation behaviour against a range of solvents across the polarity spectrum. A weighed amount of the compound was mixed with the dicarboxylic acid and the resulting mixture either warmed to 80 ^{o}C and allowed to cool under ambient conditions, or the mixture was sonicated at room temperature, or simple manually agitated. Gel formation was characterised by a simple vial inversion test; if the solvent was fully immobilised it was considered to have gelled (G). When the gelator formed weak gels by immobilizing the solvent at this stage, it was denoted "WG". The term partial gel (PG) was ascribed to samples where only partial trapping of the solvent occurred. The systems in which only precipitate, viscous solution, turbid solution or an insoluble system remained until the end of the tests were referred to as P, VS, TUS and I respectively. It was noted that precipitate systems formed by sonication were different from those formed by warming and cooling process: in the sonication process, precipitates formed immediately from the turbid solution, whereas heating led to a clear solution, and a precipitate was formed only after cooling to room temperature. Fourier transform infrared spectra were recorded with a Perkin Elmer Spectrum 100 ATR instrument. For each spectrum, 16 scans were conducted over a spectral range of 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. Rheology experiments were

performed using a TA Instruments Advanced Rheometer 2000 (shear-controlled mode). Measurements of the gels were made on a 25 mm rough-surface steel plate with a gap of 1000 μm and 2 ml of sample. The stress sweep was chosen to examine the liner viscoelasticity region (LVER) and dynamic stress yield values of the tested gel samples (Angular frequency = 6.26 rad/s, oscillatory stress = 0.1-10000.0 Pa). A constant oscillatory shear stress within the LVER (10.0 Pa) was applied to monitor the dependences of formed gels on angle frequency (6.28-628.0 rad/s). Complex viscosity was calculated from frequency sweep measurements by the formula ($|Complex\ viscosity| = \sqrt{\frac{G'^2+G''^2}{\omega^2}}$),[63] and showed that the tested gel systems were shear thinning. The rheological measurements were carried out after stabilizing the gels for 60 min in the sample holder at room temperature (25 ^{o}C). Thixotropic measurements were conducted over five cycles, with two steps per cycle as follows:[64] (a) stress sweep (deformation process, 0.1-10000.0 Pa, angle frequency=6.28 rad/s) and (b) time sweep (formation process from destroyed state, oscillatory stress = 10.0 Pa, and time = 1200 s). Recovery of thixotropic properties after destruction of the gels by manual shaking was monitored using the time sweep of the rheological oscillation mode (oscillatory stress = 10.0 Pa, t = 3600 s, angular frequency = 6.28 rad/s). Micro-morphologies of dried hydrogels were examined using Helios NanoLab DualBeam (FIB/SEM) microscope after being coated with 20 nm Au/Pd, and all the samples were generally analysed using between 1.5-3 keV, low current and in immersion mode for high resolution. ^{1}H or ^{13}C NMR and temperature-dependent NMR spectroscopic measurements were carried out on a Bruker Avance-400 and Varian Inova-500 instrument, respectively. In titration experiments, stock solutions of the urea gelator were prepared by dissolving an amount of **2a** in d^6-DMSO (namely S1, 3.28×10^{-5} mol/0.5 ml). And selected dicarboxylic acids or 20% DCl/D_2O were dissolved with the appropriate volume of the S1 solution to get the right concentration of the titrant under 10 min sonication (namely S2 and S3, $C_{free\ acid}$=18.62×10^{-5} and 22.96×10^{-5} mol/0.5 ml, respectively) Aliquots of the latter solution (S2 or S3) were added to the solution (S1) which contains **2a** without having to consider any dilution effects on the titrated species (*c.f.* Figure S9-S11).[65] For the experiments shown in Figure 6 the fresh gel of **2a**·oxalic acid (1:1), the resulting sol from sonication, and the recovered hydrogel from the sol from sonication were frozen in liquid N_2 for five minutes, and then transferred quickly for efficient pumping to the dried state. Liquid N_2 freezing was to ensure that the structures of the obtained fresh gels or sol are unchanged during drying. Small pieces of the obtained dried samples were conducting on the conductive adhesive tape of the silica slice.

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Notes and references

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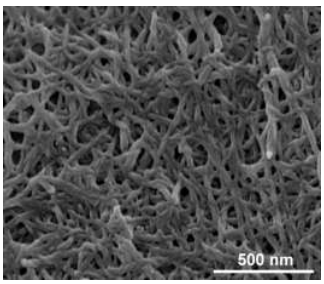
† Electronic Supplementary Information (ESI) available: Additional rheometric data, SEM images and full NMR titration and IR spectroscopic data. See DOI: 10.1039/b000000x/

1. P. Dastidar, *Chem. Soc. Rev.*, 2008, **37**, 2699-2715.
2. J. W. Steed, *Chem. Commun.*, 2011, **47**, 1379-1383.
3. G. Yu, X. Yan, C. Han and F. Huang, *Chem. Soc. Rev.*, 2013, **42**, 6697-6722.
4. A. Y.-Y. Tam and V. W.-W. Yam, *Chem. Soc. Rev.*, 2013, **42**, 1540-1567.
5. J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686-3699.
6. M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960-2004.
7. N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821-836.
8. R. G. Weiss and P. Terech (Eds.), *Molecular gels, Materials with Self-Assembled Fibrillar Networks*, Springer: Dordrecht, 2006.
9. P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133-3160.
10. A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed.*, 2008, **47**, 8002–8018.
11. D. K. Smith, in *Organic Nanostructures*, eds. J. L. Atwood and J. W. Steed, Wiley-VCH, Weinheim, 2008, pp. 111-154.
12. F. Fages (Ed.), *Top. Curr. Chem.*, 2005, **256**, 1-275.
13. Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara and T. Aida, *Nature*, 2010, **463**, 339-343.
14. L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201-1217.
15. J. J. Panda, A. Mishra, A. Basu and V. S. Chauhan, *Biomacromolecules*, 2008, **9**, 2244-2250.
16. H. H. Tonnesen and J. Karlsen, *Drug Dev. Ind. Pharm.*, 2002, **28**, 621-630.
17. Z. Yang, K. Xu, L. Wang, H. Gu, H. Wei, M. Zhang and B. Xu, *Chem. Commun.*, 2005, 4414-4416.
18. C. S. Love, V. Chechik, D. K. Smith, K. Wilson, I. Ashworth and C. Brennan, *Chem. Commun.*, 2005, 1971-1973.
19. I. A. Coates and D. K. Smith, *Chem.-Eur. J.*, 2009, **15**, 6340-6344.
20. M. Llusar and C. Sanchez, *Chem. Mat.*, 2008, **20**, 782-820.
21. F. X. Simon, N. S. Khelfallah, M. Schmutz, N. Diaz and P. J. Mesini, *J. Am. Chem. Soc.*, 2007, **129**, 3788-3789.
22. J. H. van Esch and B. L. Feringa, *Angew. Chem.-Int. Ed.*, 2000, **39**, 2263-2266.
23. A. F. Armington and J. J. O'Connor, *Inorg. Synth.*, 1980, **20**, 1-11.
24. H. K. Henisch, *Crystal Growth in Gels*, The Pennsylvania State University Press, University Park, PA, 1976.
25. L. E. Buerkle and S. J. Rowan, *Chem. Soc. Rev.*, 2012, **41**, 6089-6102.
26. A. R. Hirst and D. K. Smith, *Chem.-Eur. J.*, 2005, **11**, 5496-5508.
27. M. M. Smith and D. K. Smith, *Soft Matter*, 2011, **7**, 4856-4860.
28. D. M. Ryan, T. M. Doran and B. L. Nilsson, *Langmuir*, 2011, **27**, 11145-11156.
29. I. Kapoor, E. M. Schon, J. Bachl, D. Kuhbeck, C. Cativiela, S. Saha, R. Banerjee, S. Roelens, J. J. Marrero-Tellado and D. D. Diaz, *Soft Matter*, 2012, **8**, 3446-3456.
30. B. Adhikari, J. Nanda and A. Banerjee, *Soft Matter*, 2011, **7**, 8913-8922.
31. D. G. Velazquez, D. D. Diaz, A. G. Ravelo and J. J. M. Tellado, *J. Am. Chem. Soc.*, 2008, **130**, 7967-7973.
32. K. L. Morris, L. Chen, J. Raeburn, O. R. Sellick, P. Cotanda, A. Paul, P. C. Griffiths, S. M. King, R. K. O'Reilly, L. C. Serpell and D. J. Adams, *Nature Commun.*, 2013, **4**.
33. F. Fages, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1680-1682.
34. G. O. Lloyd and J. W. Steed, *Nature Chem.*, 2009, **1**, 437-442.
35. H. Maeda, *Chem. Eur. J.*, 2008, **36**, 11274-11282.
36. J. E. A. Webb, M. J. Crossley, P. Turner and P. Thordarson, *J. Am. Chem. Soc.*, 2007, **129**, 7155-7162.
37. P. Byrne, D. R. Turner, G. O. Lloyd, N. Clarke and J. W. Steed, *Cryst. Growth Des.*, 2008, **8**, 3335-3344.

38. P. Byrne, G. O. Lloyd, L. Applegarth, K. M. Anderson, N. Clarke and J. W. Steed, *New J. Chem.*, 2010, **34**, 2261-2274.
39. B. Wu, X. Huang, Y. Xia, X.-J. Yang and C. Janiak, *CrystEngComm*, 2007, **9**, 676-685.
40. L. S. Reddy, S. Basavoju, V. R. Vangala and A. Nangia, *Cryst. Growth Des.*, 2005, **6**, 161-173.
41. M. C. Etter, Z. Urbanczyklipkowska, M. Ziaebrahimi and T. W. Panunto, *J. Am. Chem. Soc.*, 1990, **112**, 8415-8426.
42. F. S. Schoonbeek, J. H. van Esch, R. Hulst, R. M. Kellogg and B. L. Feringa, *Chem.-Eur. J.*, 2000, **6**, 2633-2643.
43. J. H. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg and B. L. Feringa, *Chem. Eur. J.*, 1999, **5**, 937-950.
44. M.-O. M. Piepenbrock, N. Clarke and J. W. Steed, *Soft Matter*, 2011, **7**, 2412–2418.
45. M.-O. M. Piepenbrock, N. Clarke and J. W. Steed, *Soft Matter*, 2010, **6**, 3541–3547.
46. M.-O. M. Piepenbrock, N. Clarke and J. W. Steed, *Langmuir*, 2009, **25**, 8451-8456.
47. L. Meazza, J. A. Foster, K. Fucke, P. Metrangolo, G. Resnati and J. W. Steed, *Nature Chem.*, 2013, **5**, 42-47.
48. N. N. Adarsh, D. K. Kumar and P. Dastidar, *Tetrahedron*, 2007, **63**, 7386-7396.
49. L. A. Estroff and A. D. Hamilton, *Angew. Chem., Int. Ed.*, 2000, **39**, 3447-3450.
50. E. Ostuni, P. Kamaras and R. G. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1324-1326.
51. G. O. Lloyd and J. W. Steed, *Soft Matter*, 2011, **7**, 75-84.
52. L. Applegarth, N. Clarke, A. C. Richardson, A. D. M. Parker, I. Radosavljevic-Evans, A. E. Goeta, J. A. K. Howard and J. W. Steed, *Chem. Commun.*, 2005, 5423-5425.
53. V. Percec, M. Peterca, M. E. Yurchenko, J. G. Rudick and P. A. Heiney, *Chem.-Eur. J.*, 2008, **14**, 909-918.
54. W. G. Weng, A. M. Jamieson and S. J. Rowan, *Tetrahedron*, 2007, **63**, 7419-7431.
55. J. Delgado and R. Castillo, *J. Colloid Interf. Sci.*, 2007, **312**, 481-488, and references therein.
56. G. Schramm, *A Practical Approach to Rheology and Rheometry*, 2nd edn., Gebrueder HAAKE GmbH, Karlsruhe, 2000.
57. X. Huang, S. R. Raghavan, P. Terech and R. G. Weiss, *J. Am. Chem. Soc.*, 2006, **128**, 15341-15352.
58. A. Dawn, T. Shiraki, H. Ichikawa, A. Takada, Y. Takahashi, Y. Tsuchiya, L. T. N. Lien and S. Shinkai, *J. Am. Chem. Soc.*, 2011, **134**, 2161-2171.
59. W. M. Haynes, ed., *CRC Handbook of Chemistry and Physics*, 92nd edn., Taylor and Francis, Boca Raton, 2011.
60. T. W. G. Solomons, in *Organic Chemistry*, John Wiley & Sons, New York, 3rd edn., 1984, p. 787.
61. G. K. S. Ooi and R. J. Magee, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3315-3320.
62. D. R. Turner, M. J. Paterson and J. W. Steed, *Chem. Commun.*, 2008, 1395-1397.
63. X. Chen, K. Liu, P. He, H. Zhang and Y. Fang, *Langmuir*, 2012, **28**, 9275-9281.
64. X. Cai, K. Liu, J. Yan, H. Zhang, X. Hou, Z. Liu and Y. Fang, *Soft Matter*, 2012, **8**, 3756-3761.
65. K. Hirose, ed. C. A. Schalley, Wiley-VCH, Weinheim, 2007, p. 41.

Graphical Abstract

Two component thixotropic co-gels arise from rapid precipitation leading to fibre assembly



Triggered Formation of Thixotropic Hydrogels by Balancing Competitive Supramolecular Synthons

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Supplementary Material

Table S1 Gelation behaviours of **1** and **2** in polar solvents

Solvent	1a	1b	1c	1d	2a	2b	Solvent	1a	1b	1c	1d	2a	2b
H_2O	P	P	P	P	I	I	Cyclohexanone	P	P	P	P	P	G
Methanol	P	P	P	P	P	G	Cyclopentanone	P	P	P	P	P	G
Ethanol	P	P	P	P	P	G	Diethylene glycol	P	P	P	P	I	G
1-Butanol	P	P	P	P	P	G	Acetone	P	P	P	P	I	VS
2-Butanol	P	P	P	P	P	G	Acetonitrile	I	I	I	I	I	VS
1-Propanol	P	P	P	P	P	G	1,4-Dioxane	I	I	I	I	I	VS
2-Propanol	P	P	P	P	P	WG	DMF	S	S	S	S	S	S
1-Pentanol	P	P	P	P	P	G	DMSO	S	S	S	S	S	S

Table S2 Gelation behaviours of **1a** and dicarboxylic acids in polar solvents

Solvent	1a+a		1a+b		1a+c		1a+d		1a+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	I	P	P	P	P	P	P	TUS	P
Methanol	P	I	P	P	P	P	P	P	P	P
Ethanol	P	I	P	P	P	P	P	P	P	P
1-Propanol	P	I	P	P	TUS	P	P	P	P	P
2-Propanol	P	I	P	P	P	P	P	P	P	P
1-Butanol	P	I	P	P	P	P	P	P	P	P
2-Butanol	P	I	P	P	P	P	P	P	P	P
1-Pentanol	P	I	P	P	P	P	P	P	P	P
Cyclohexanone	P	I	P	I	P	I	P	I	P	P
Cyclopentanone	P	I	P	P	P	P	P	P	P	P
Diethylene glycol	VS	TUS	P	S	P	S	S	S	S	S
Acetone	P	I	P	I	P	I	P	I	P	I
Acetonitrile	P	I	P	I	P	I	P	I	P	I
1,4-Dioxane	P	I	P	I	P	I	P	I	P	I
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	1a+f		1a+g		1a+h		1a+i		1a+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	P	P	P	P	P	P	R	P	P
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	P	P	P	P	P	P	P	P	P	P
2-Butanol	TUS	P	P	P	P	P	P	P	P	P
1-Propanol	P	P	P	P	P	P	P	P	P	P
2-Propanol	P	P	P	P	P	P	P	P	P	P
1-Pentanol	P	P	P	P	P	P	P	P	P	P
Cyclohexanone	P	I	P	I	P	I	P	I	P	I
Cyclopentanone	P	P	P	P	P	P	P	P	P	P
Diethylene glycol	TUS	S	S	S	S	S	S	S	P	S
Acetone	P	I	P	I	P	I	P	I	P	I
Acetonitrile	P	I	P	I	P	I	P	I	P	I
1,4-Dioxane	P	I	P	I	P	I	P	I	P	I
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Table S3 Gelation behaviours of **1b** and dicarboxylic acids in polar solvents

Solvent	1b+a		1b+b		1b+c		1b+d		1b+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	TUS	I	TUS	P	P	P	P	P	P	P
Methanol	P	P	P	P	TUS	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	P	P	P	P	P	P	P	P	P	P
2-Butanol	P	P	P	P	P	P	P	P	P	P
1-Propanol	TUS	I	TUS	P	TUS	P	P	P	P	P
2-Propanol	TUS	I	P	TUS	P	P	P	TUS	P	P
1-Pentanol	TUS	I	P	P	TUS	P	P	P	P	P
Cyclohexanone	P	I	P	I	P	I	P	I	P	TUS
Cyclopentanone	P	I	P	TUS	P	P	P	P	P	P
Diethylene glycol	VS	TUS	S	S	S	S	S	S	S	S
Acetone	P	I	P	TUS	TUS	P	TUS	P	P	P
Acetonitrile	P	I	P	P	TUS	P	P	P	P	P
1,4-dioxane	P	I	P	P	TUS	P	P	VS	P	P
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	1b+f		1b+g		1b+h		1b+i		1b+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	P	P	P	P	R	P	R	P	TUS
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	G	P	P	P	P	P	P	P	P	P
2-Butanol	TUS	P	P	P	P	P	P	P	P	P
1-Propanol	G	P	P	P	P	P	P	P	P	P
2-Propanol	G	P	P	P	P	P	P	P	P	P
1-Pentanol	PG	P	P	P	P	P	P	P	P	P
Cyclohexanone	P	I	P	I	P	I	P	I	P	I
Cyclopentanone	P	P	TUS	VS	P	P	P	P	P	P
Diethylene glycol	S	S	S	S	S	S	S	S	S	S
Acetone	P	P	P	P	P	P	P	P	P	I
Acetonitrile	P	P	P	P	P	P	P	P	P	TUS
1,4-Dioxane	P	P	P	P	P	P	P	P	P	TUS
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Table S4 Gelation behaviours of **1c** and dicarboxylic acids

Solvent	1c+a		1c+b		1c+c		1c+d		1c+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	P	P	P	P	P	P	P	P	P
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	P	P	P	P	P	P	P	P	P	R
2-Butanol	P	P	P	P	P	P	P	P	P	P
1-Propanol	P	P	P	P	P	P	P	P	P	P
2-Propanol	P	P	P	R	P	P	P	P	P	P
1-Pentanol	VS	VS	P	R	P	P	P	P	P	P
Cyclohexanone	VS	P	P	P	P	P	P	P	P	P
Cyclopentanone	P	P	P	P	P	P	P	P	P	P
Diethylene glycol	TUS	S	TUS	S	TUS	P	S	S	TUS	S
Acetone	P	I	P	P	P	P	P	VS	P	I
Acetonitrile	P	I	P	P	P	P	P	P	P	P
1,4-dioxane	VS	TUS	P	P	P	P	P	P	P	P
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	1c+f		1c+g		1c+h		1c+i		1c+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	P	P	P	P	P	P	P	P	P
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	P	P	P	P	P	P	P	P	P	P
2-Butanol	P	P	P	P	P	P	P	P	P	P
1-Propanol	VS	P	P	P	P	P	P	P	P	P
2-Propanol	P	P	P	P	P	P	P	P	P	P
1-Pentanol	P	P	P	P	P	R	P	P	P	P
Cyclohexanone	P	P	P	P	P	I	P	I	P	I
Cyclopentanone	P	P	P	P	P	P	P	P	P	P
Diethylene glycol	P	S	TUS	S	TUS	TUS	P	P	TUS	S
Acetone	P	P	P	P	P	P	P	P	P	P
Acetonitrile	P	P	P	P	P	P	P	P	P	P
1,4-Dioxane	P	P	P	P	P	P	P	P	P	P
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Table S5 Gelation behaviours of **1d** and dicarboxylic acids

Solvent	1d+a		1d+b		1d+c		1d+d		1d+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	VS	P	TUS	P	TUS	P	TUS	P	TUS	VS
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	P	P	P	P	P	P	P	P	P	P
2-Butanol	VS	P	P	P	P	P	P	P	P	VS
1-Propanol	VS	P	P	P	P	P	P	P	P	P
2-Propanol	VS	P	P	P	P	P	P	P	P	P
1-Pentanol	VS	P	P	P	P	P	P	P	P	P
Cyclohexanone	TUS	VS	P	P	P	P	P	P	P	P
Cyclopentanone	P	TUS	P	P	P	P	P	P	P	P
Diethylene glycol	TUS	P	TUS	VS	TUS	VS	TUS	VS	TUS	P
Acetone	P	P	P	P	P	P	P	P	P	P
Acetonitrile	P	P	P	P	P	P	P	P	P	P
1, 4-Dioxane	VS	P	P	P	P	P	P	P	P	P
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	1d+f		1d+g		1d+h		1d+i		1d+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	P	P	TUS	TUS	TUS	I	P	P	P	I
Methanol	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P
1-Butanol	TUS	VS	P	P	P	P	P	P	TUS	P
2-Butanol	TUS	P	P	P	P	P	P	P	P	P
1-Propanol	VS	P	P	P	P	P	P	P	P	P
2-Propanol	P	P	P	P	P	P	P	P	P	P
1-Pentanol	P	P	P	P	P	P	P	P	TUS	P
Cyclohexanone	TUS	P	P	P	P	TUS	TUS	P	P	P
Cyclopentanone	TUS	P	P	P	P	P	P	P	P	P
Diethylene glycol	TUS	VS	TUS	VS	TUS	VS	TUS	VS	TUS	VS
Acetone	TUS	P	P	P	P	P	P	P	P	P
Acetonitrile	TUS	P	P	P	P	P	P	P	P	P
1, 4-Dioxane	P	P	P	P	P	P	P	P	P	P
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Table S6 Gelation behaviours of **2a** and dicarboxylic acids

Solvent	2a+a		2a+b		2a+c		2a+d		2a+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	G	I	P	TUS	VS	VS	P	I	G	I
Methanol	P	P	P	P	P	P	P	P	P	I
Ethanol	P	I	P	P	P	P	P	VS	P	I
1-Butanol	P	P	VS	P	P	P	P	P	P	P
2-Butanol	P	P	P	I	P	P	P	P	P	P
1-Propanol	P	P	P	P	P	P	P	I	P	P
2-Propanol	P	P	P	I	P	P	P	VS	P	P
1-Pentanol	P	P	P	P	P	P	P	I	P	P
Cyclohexanone	P	I	TUS	P	P	P	P	P	TUS	P
Cyclopentanone	P	I	P	P	P	P	P	P	TUS	P
Diethylene glycol	P	P	P	P	TUS	P	TUS	P	TUS	P
Acetone	P	I	P	I	P	I	P	I	P	P
Acetonitrile	P	I	P	I	P	I	P	I	P	I
1,4-Dioxane	P	I	P	I	P	I	P	I	P	I
DMF	TUS	P	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	2a+f		2a+g		2a+h		2a+i		2a+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	VS	I	P	P	P	P	P	P	G	P
Methanol	P	I	P	P	P	I	P	I	P	P
Ethanol	P	P	P	I	P	P	P	P	P	P
1-Butanol	VS	VS	P	I	P	P	I	I	P	P
2-Butanol	P	I	P	TUS	TUS	P	TUS	P	P	P
1-Propanol	P	I	P	P	P	I	P	P	P	P
2-Propanol	P	VS	P	P	P	P	P	P	P	P
1-Pentanol	P	P	P	P	P	I	P	I	P	P
Cyclohexanone	TUS	I	P	P	P	P	P	P	P	P
Cyclopentanone	TUS	P	P	P	P	P	P	P	P	P
Diethylene glycol	TUS	S	S	S	TUS	P	TUS	P	P	P
Acetone	TUS	I	P	I	P	I	P	I	P	I
Acetonitrile	TUS	I	P	I	P	I	P	I	P	I
1,4-Dioxane	P	I	P	I	P	I	P	I	P	I
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Table S7 Gelation behaviours of **2b** and dicarboxylic acids

Solvent	2b+a		2b+b		2b+c		2b+d		2b+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	VS	I	PG	I	P	I	G	I	G	I
Methanol	-	-	-	-	-	-	-	-	-	-
Ethanol	-	-	-	-	-	-	-	-	-	-
1-Butanol	-	-	-	-	-	-	-	-	-	-
2-Butanol										
1-Propanol	-	-	-	-	-	-	-	-	-	-
2-Propanol	-	-	-	-	-	-	-	-	-	-
1-Pentanol	-	-	-	-	-	-	-	-	-	-
Cyclohexanone	-	-	-	-	-	-	-	-	-	-
Cyclopentanone	-	-	-	-	-	-	-	-	-	-
Diethylene glycol	-	-	-	-	-	-	-	-	-	-
Acetone	P	I	G	G	G	G	P	G	G	VS
Acetonitrile	P	I	P	G	PG	PG	G	PG	P	I
1,4-dioxane	P	P	G	VS	G	VS	G	VS	G	VS
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	2b+f		2b+g		2b+h		2b+i		2b+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H_2O	VS	I	TUS	I	VS	I	VS	I	P	I
CH_3OH	-	-	-	-	-	-	-	-	-	-
CH_3CH_2OH	-	-	-	-	-	-	-	-	-	-
1-Butanol	-	-	-	-	-	-	-	-	-	-
2-Butanol										
1-Propanol	-	-	-	-	-	-	-	-	-	-
2-Propanol	-	-	-	-	-	-	-	-	-	-
1-Pentanol	-	-	-	-	-	-	-	-	-	-
Cyclohexanone	-	-	-	-	-	-	-	-	-	-
Cyclopentanone	-	-	-	-	-	-	-	-	-	-
Diethylene glycol	-	-	-	-	-	-	-	-	-	-
Acetone	PG	I	TUS	I	G	I	VS	VS	P	I
Acetonitrile	G	P	TUS	TUS	G	VS	P	I	P	I
1,4-Dioxane	P	P	P	P	VS	I	P	I	P	I
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Notes: "-" referred to the gel systems of pure **2b** without any dicarboxylic acid

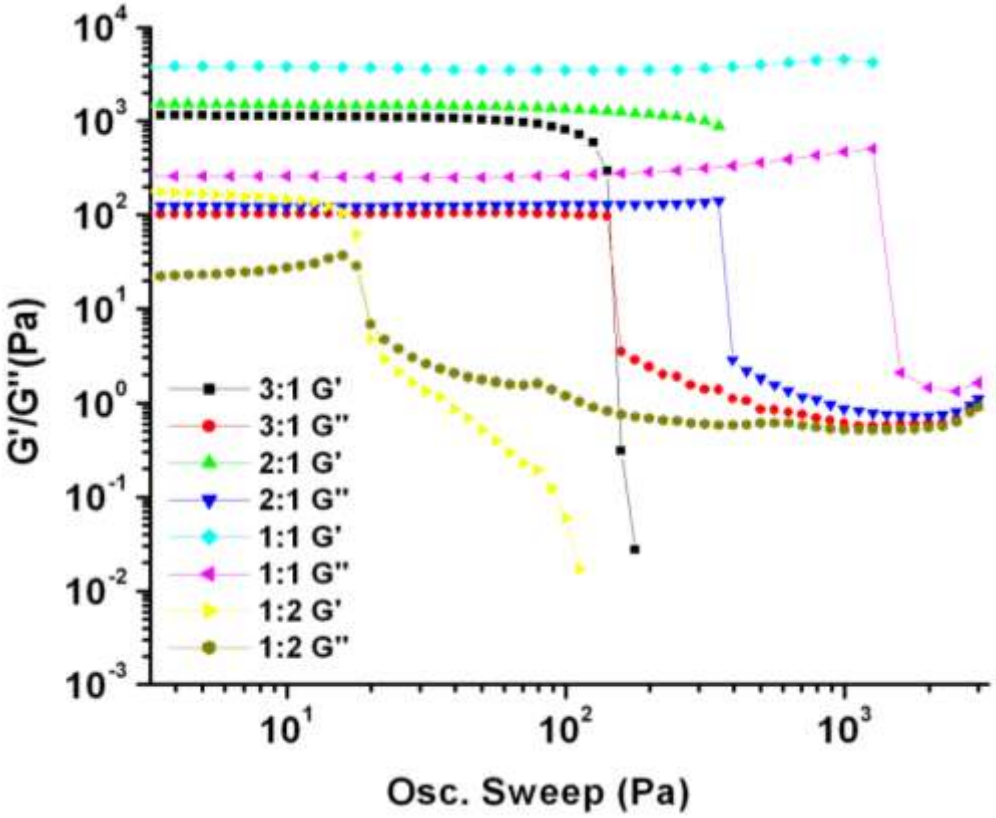


Figure S1 Stress sweeps of **2a**/oxalic acid hydrogels at different ratios (2.0 wt/vol %)

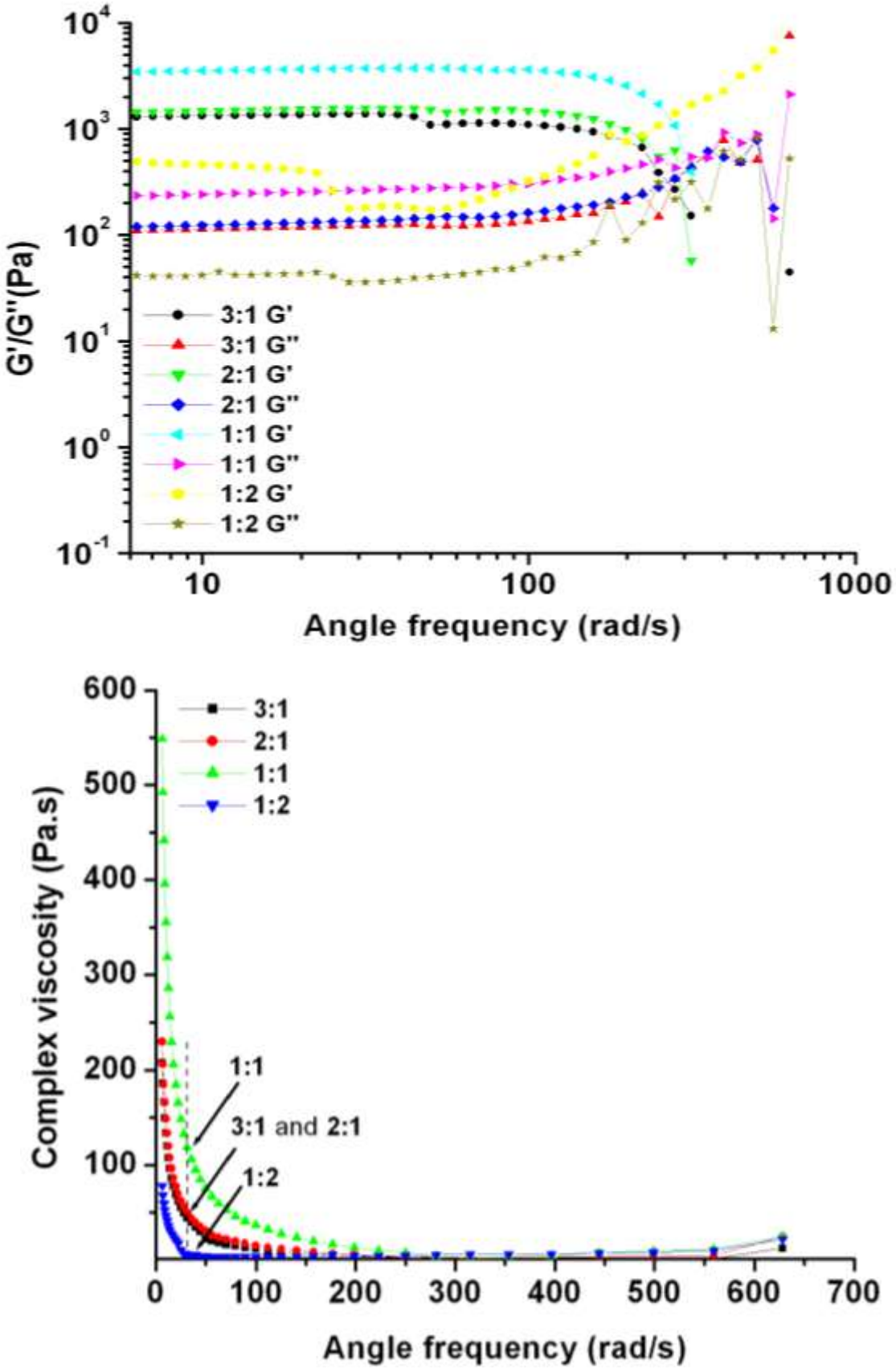


Figure S2 Angle frequency sweep (top) and complex viscosity (bottom) of supramolecular gels at different ratio (3:1, 2:1, 1:1 and 1:2) between **2a** and oxalic acid in water

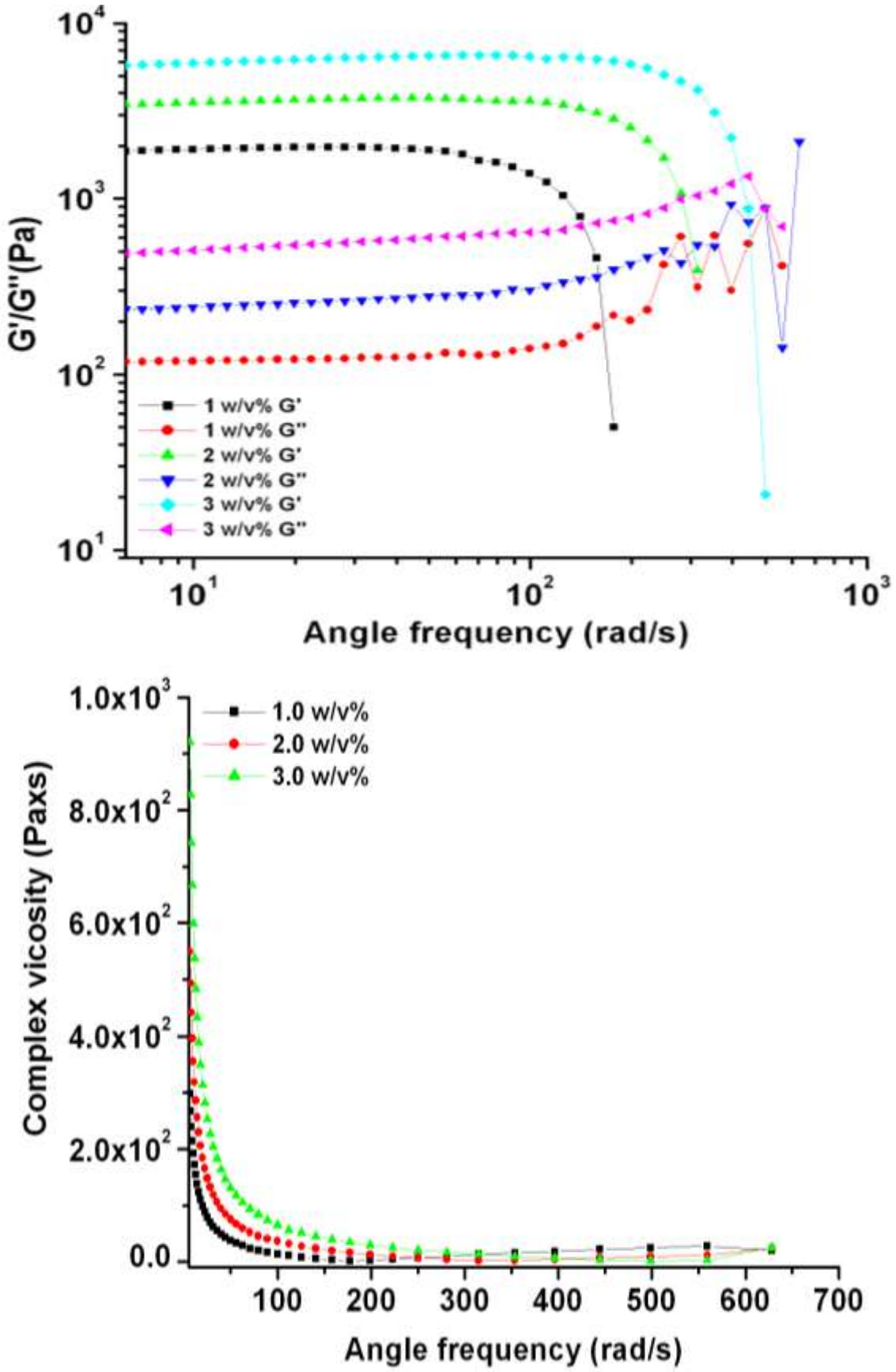


Figure S3 Angle frequency sweep (top) and complex viscosity (bottom) of supramolecular gels of **2a** and oxalic acid at different concentration (1:1 ratio)

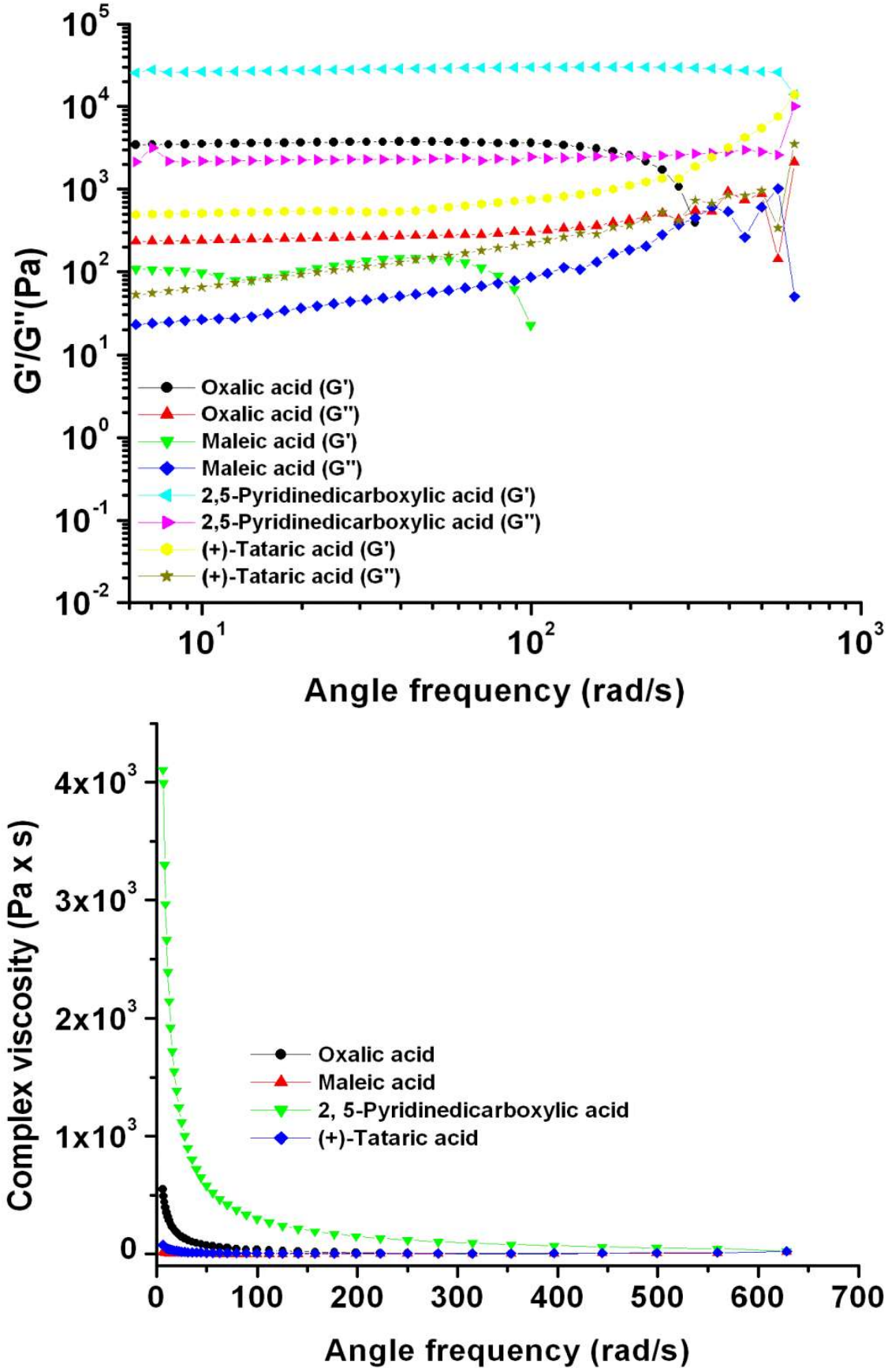


Figure S4 Angle frequency sweep (top) and complex viscosity (bottom) of hydrogels of different dicarboxylic acid systems (1:1, 2.0 w/v%)

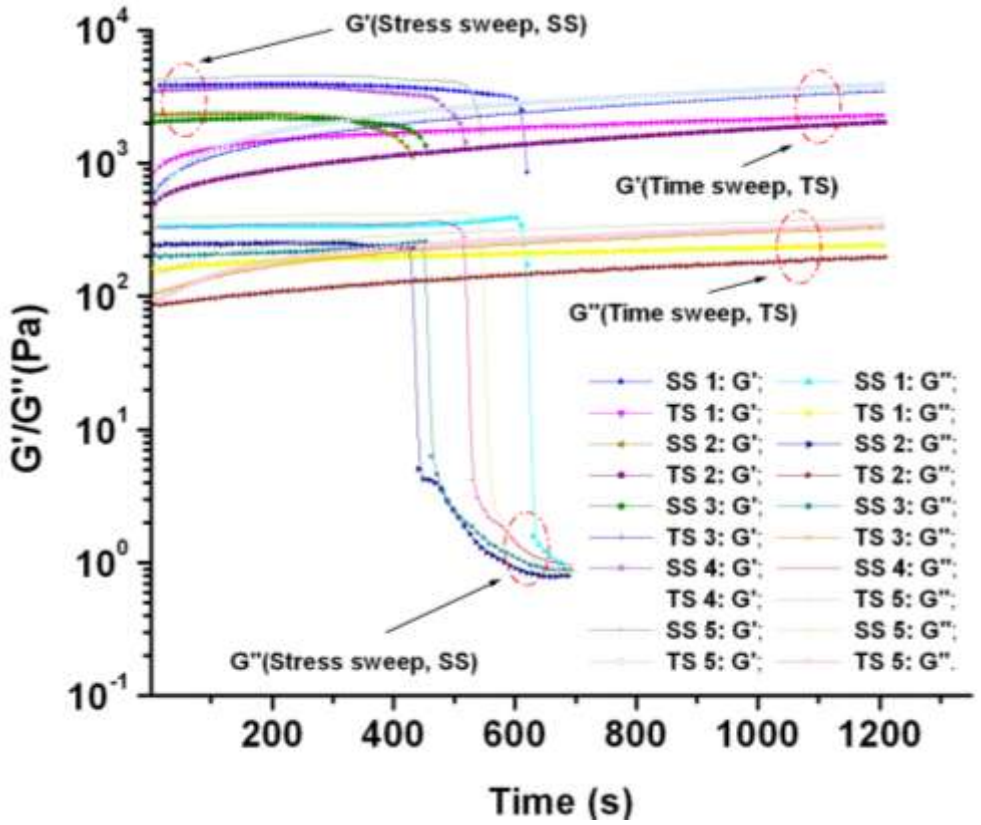


Figure S5 Five cycles of stress sweep (deformation, SS) and time sweep (formation, TS) for the **2a**·oxalic acid hydrogel (1:1, 2.0 w/v%)

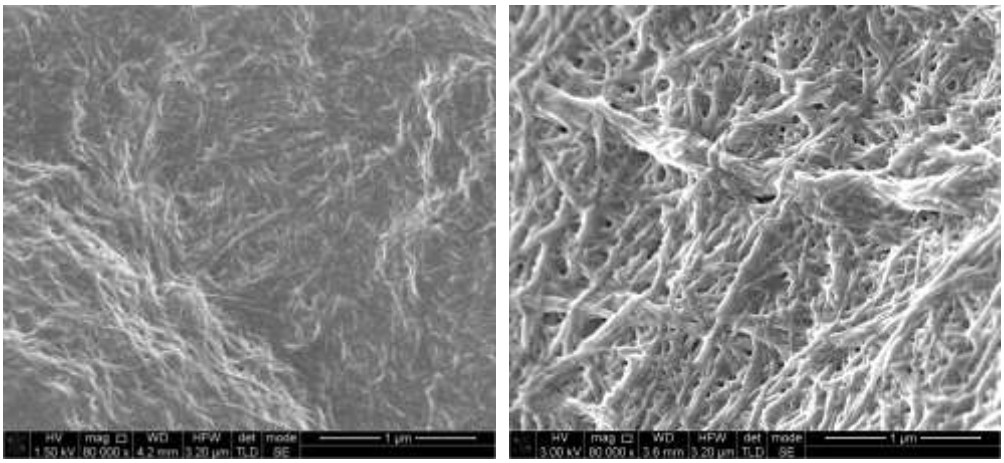


Figure S6 Morphologies of dried hydrogels of **2a**/oxalic acid (1:1) at concentrations of (left) 1.0 w/v% and (right) 3.0 w/v%

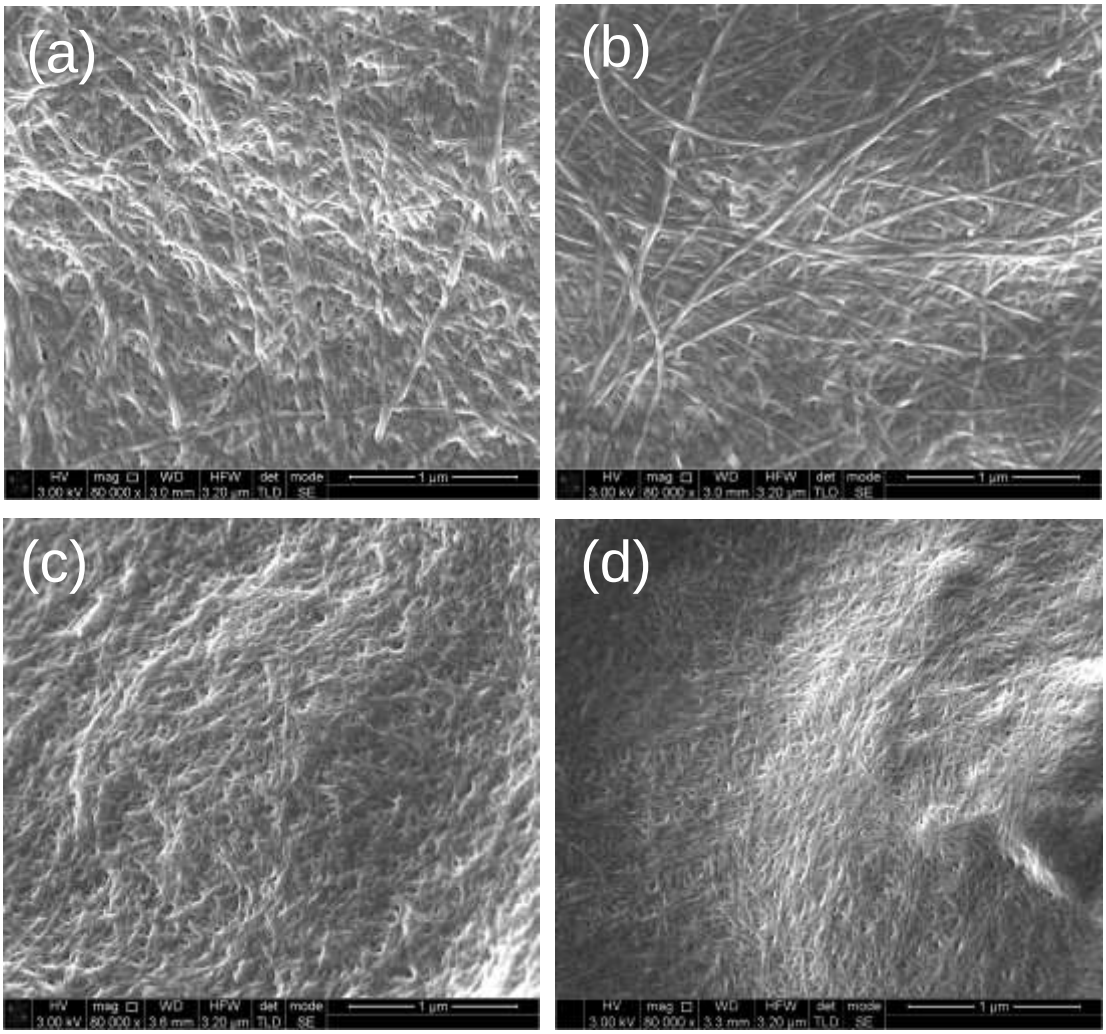


Figure S7 Morphologies of dried hydrogels of **2a**/oxalic acid (a), maleic acid (b), 2,5-pyridinecarboxylic acid (c) and (+)-tartaric acid (d) at 2.0 w/v% (1:1 ratio)

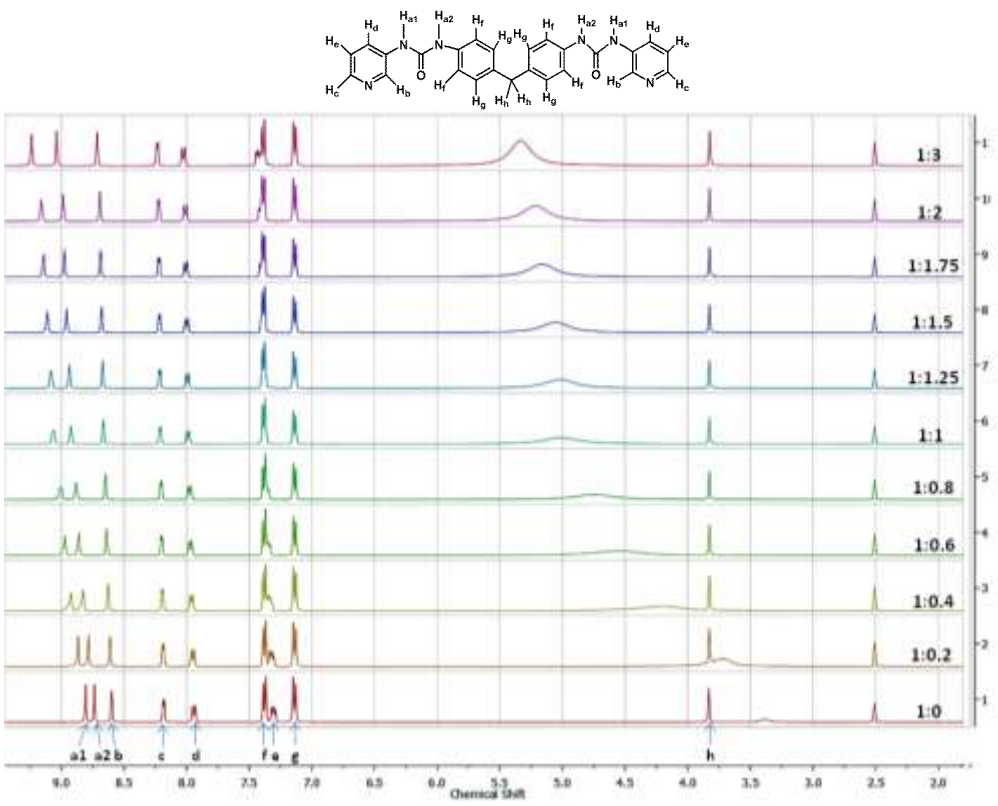


Figure S8 [1]H NMR spectroscopic titration of oxalic acid into **2a**/d6-DMSO solution

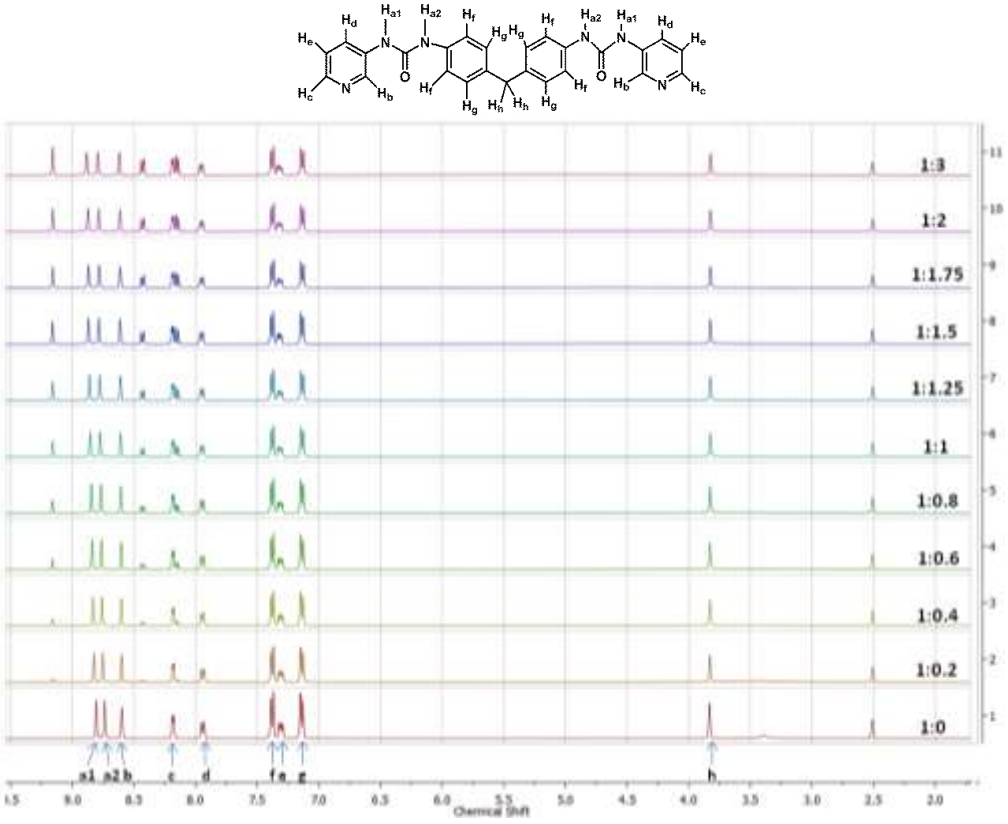


Figure S9 [1]H NMR spectroscopic titration of 2, 5-pyridinedicarboxylic acid into **2a**/d^6-DMSO solution

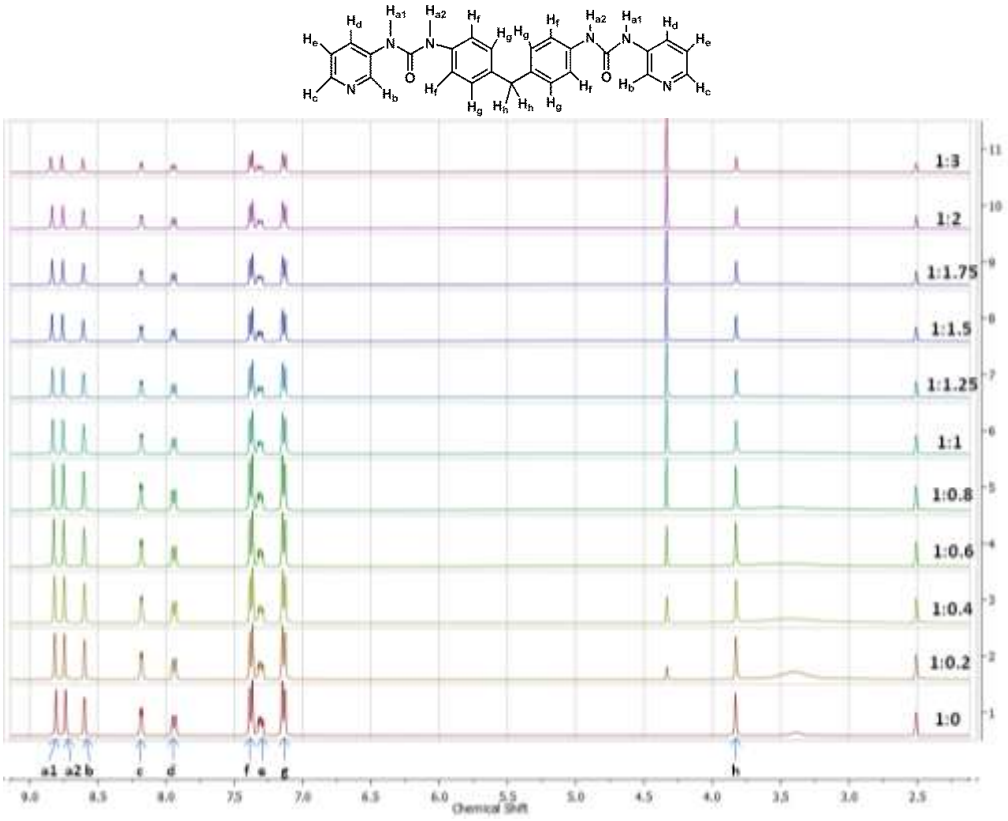


Figure S10 ^{1}H NMR spectroscopic titration of (+)-tartaric acid into **2a**/d^{6}-DMSO solution

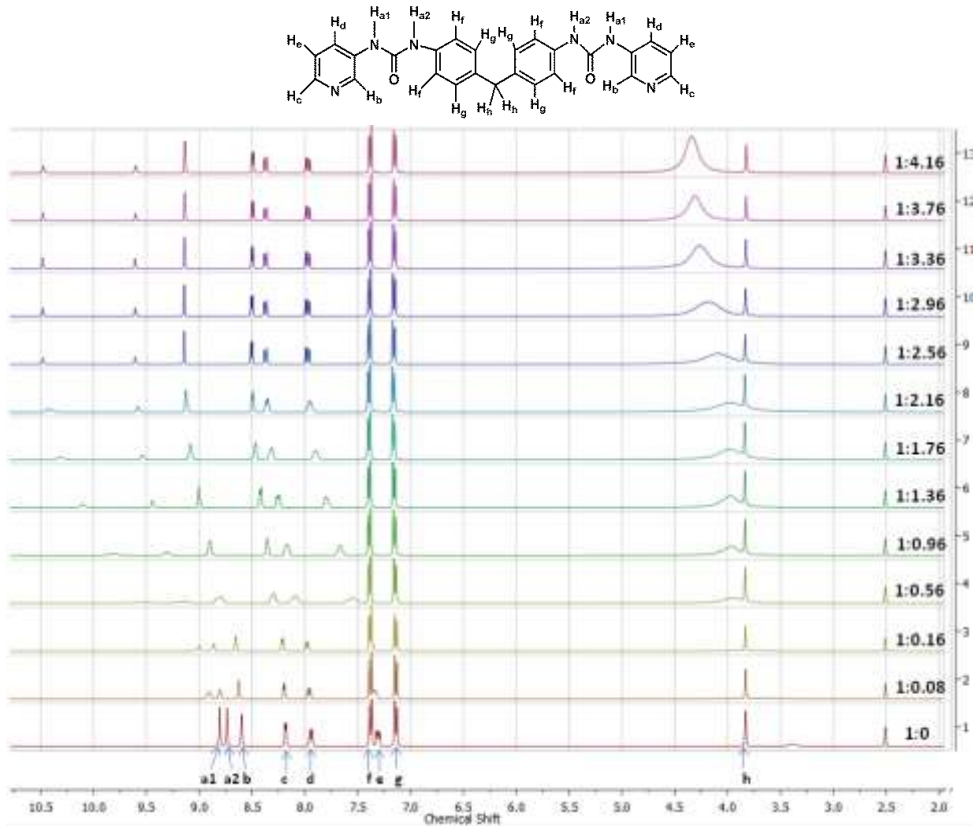


Figure S11 ^{1}H NMR spectroscopic titration of DCl into **2a**/d^{6}-DMSO solution

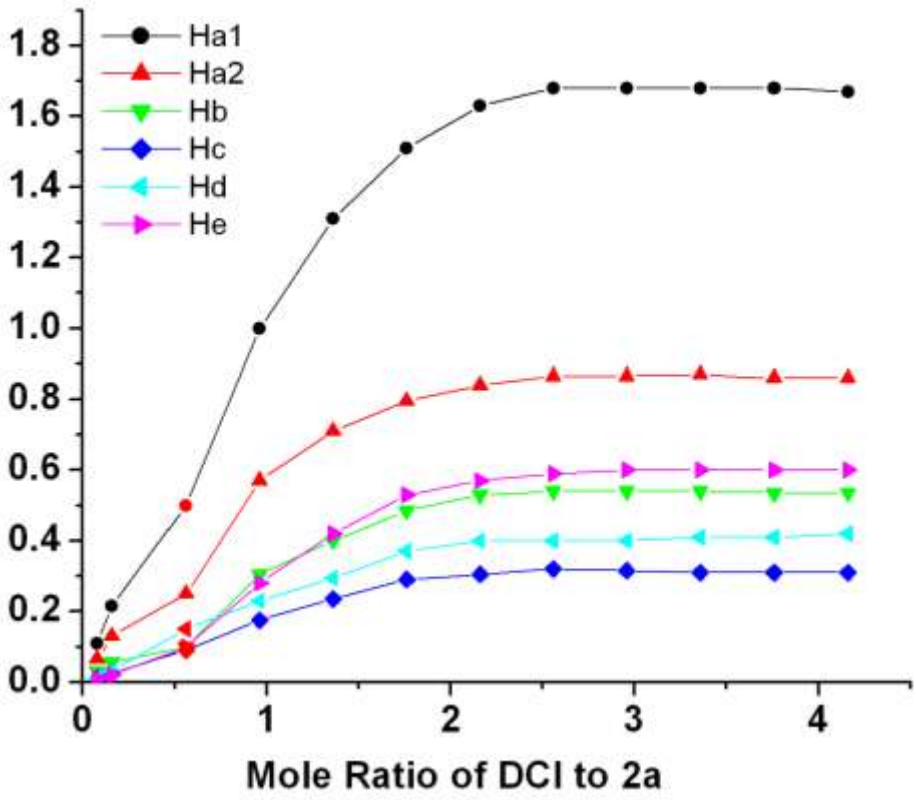


Figure S12 Dependence of chemical shift on mole ratio of DCl to **2a** in d^6-DMSO

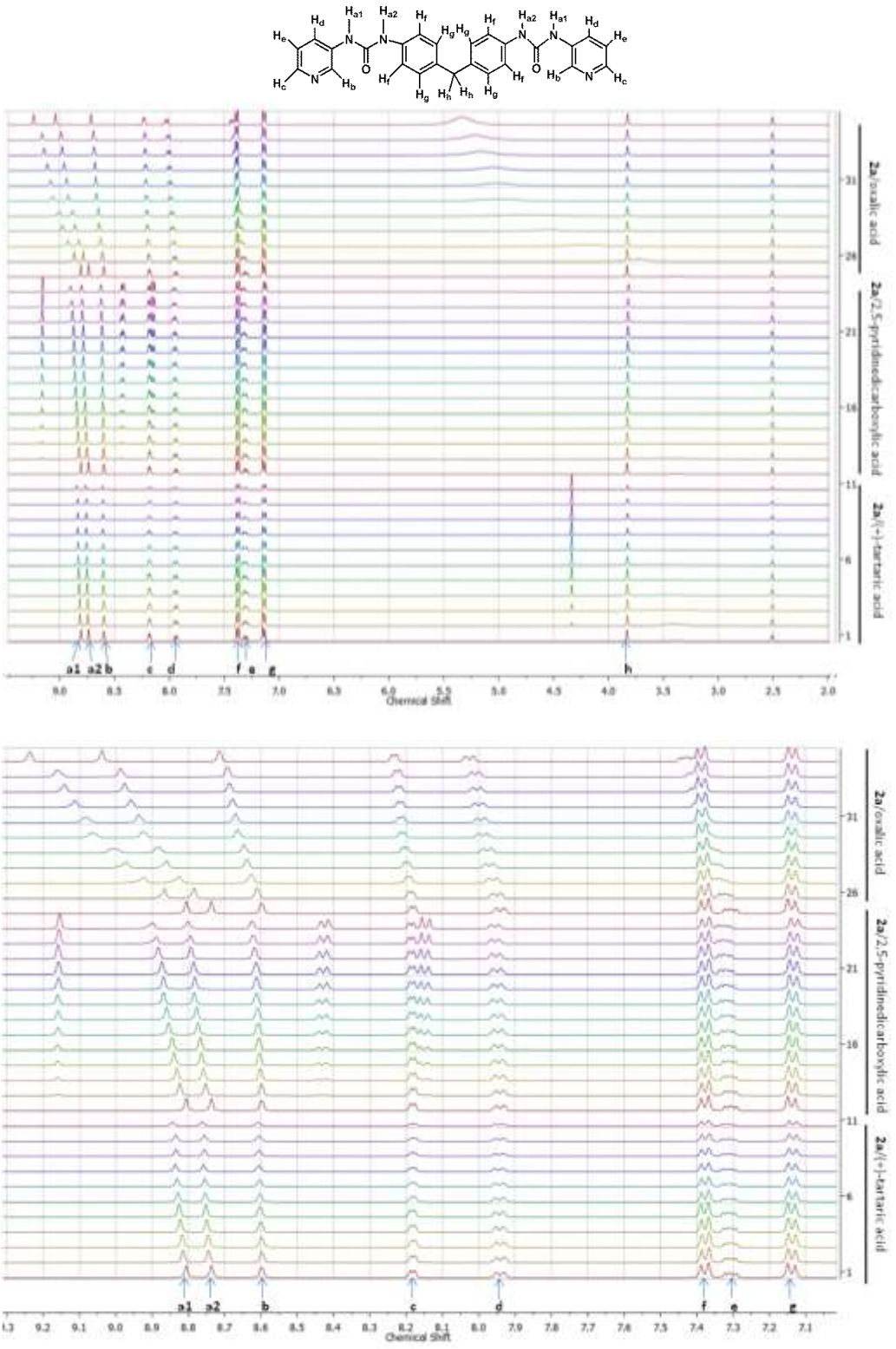


Figure S13 ^{1}H NMR spectroscopic titration of oxalic acid, (+)-tartaric acid, and 2, 5-pyridinedicarboxylic acid into **2a**/d^{6}-DMSO solution

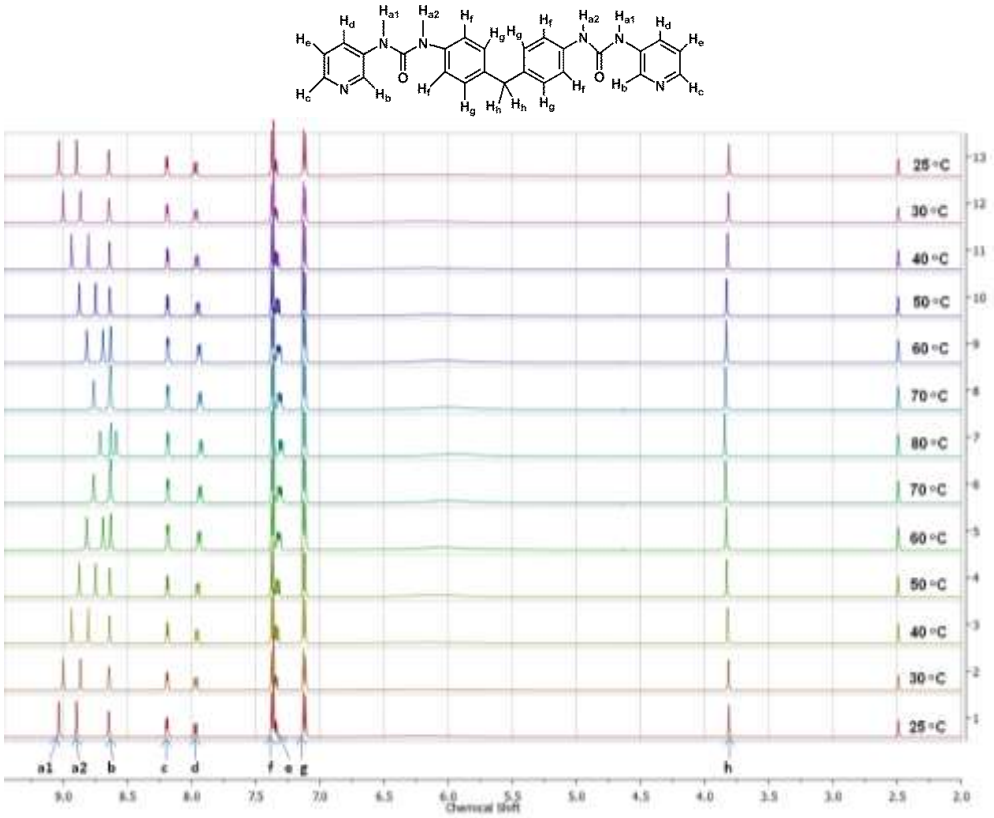


Figure S14 Temperature-dependent ^{1}H NMR spectra of **2a**/oxalic acid in d^{6}-DMSO (ratio is 1:1, temperature is change 25 ^{o}C to 80 ^{o}C, and then down to 25 ^{o}C)

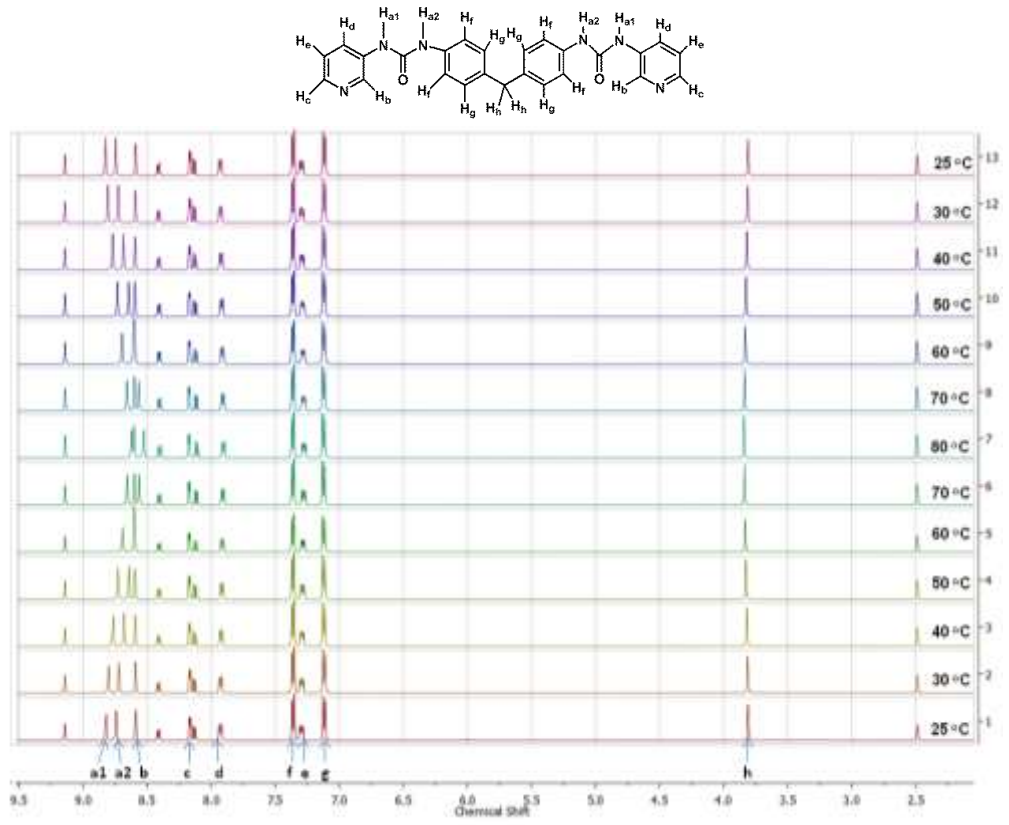


Figure S15 Temperature-dependent ^{1}H NMR spectra of **2a**/2, 5-pyridinedicarboxylic acid in d^{6}-DMSO (ratio is 1:1, temperature is change 25 ^{o}C to 80 ^{o}C, and then down to 25 ^{o}C)

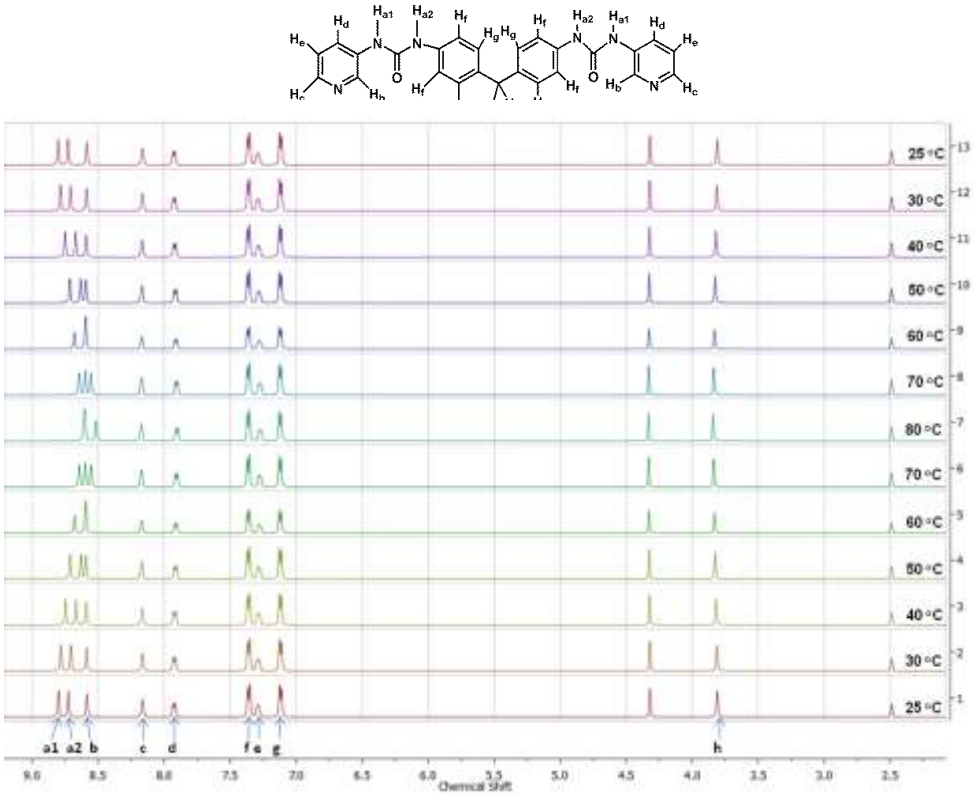


Figure S16 Temperature-dependent ^{1}H NMR spectra of **2a**/(+)-tartaric acid in d^{6}-DMSO (ratio is 1:1, temperature is change 25 ^{o}C to 80 ^{o}C, and then down to 25 ^{o}C)

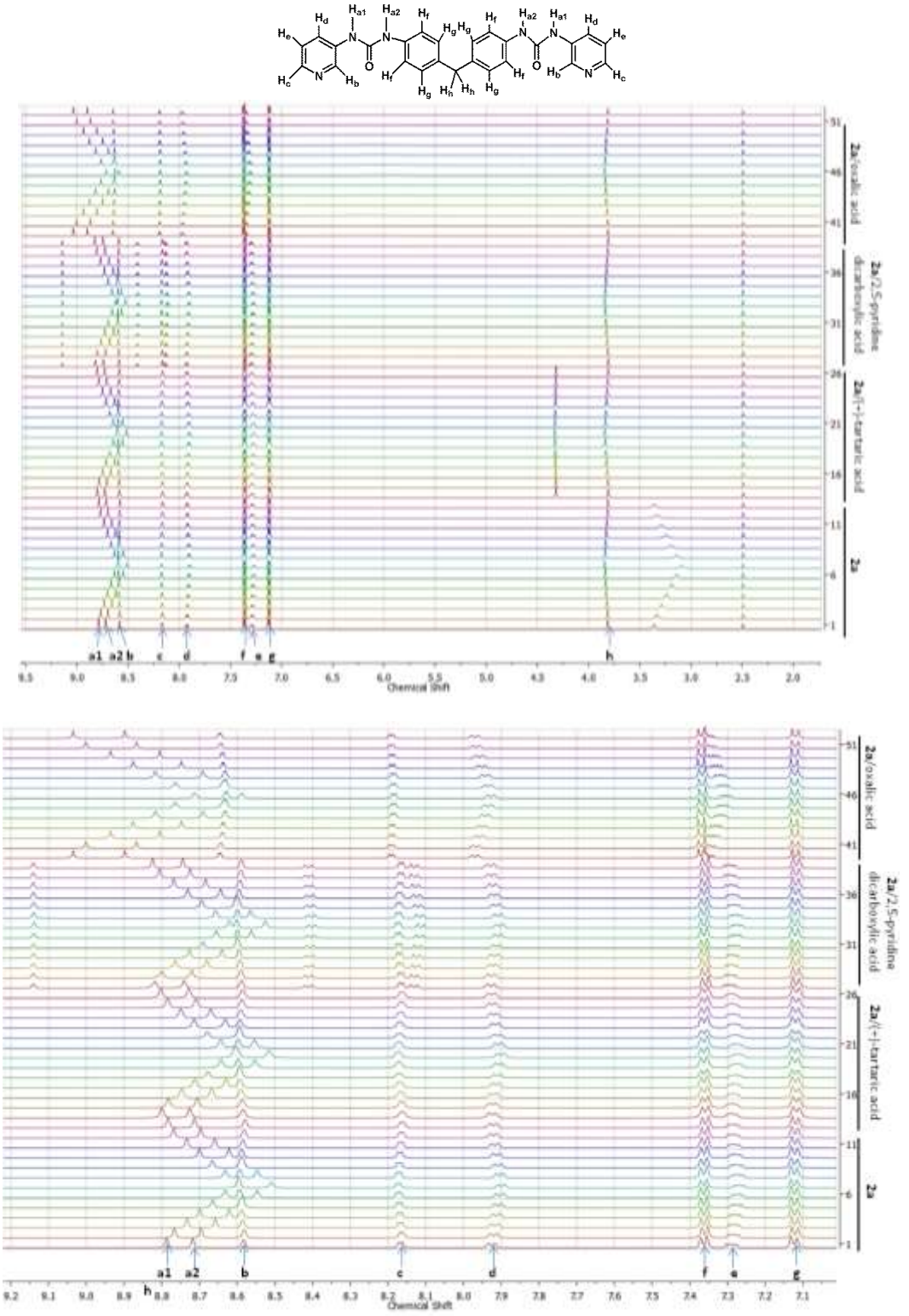


Figure S17 Temperature-dependent ^{1}H NMR spectra of **2a**/oxalic acid, 2, 5-pyridinedicarboxylic acid and (+)-tartaric acid in d^6-DMSO (ratio is 1:1, temperature is change 25 ^{o}C to 80 ^{o}C, and then down to 25 ^{o}C)

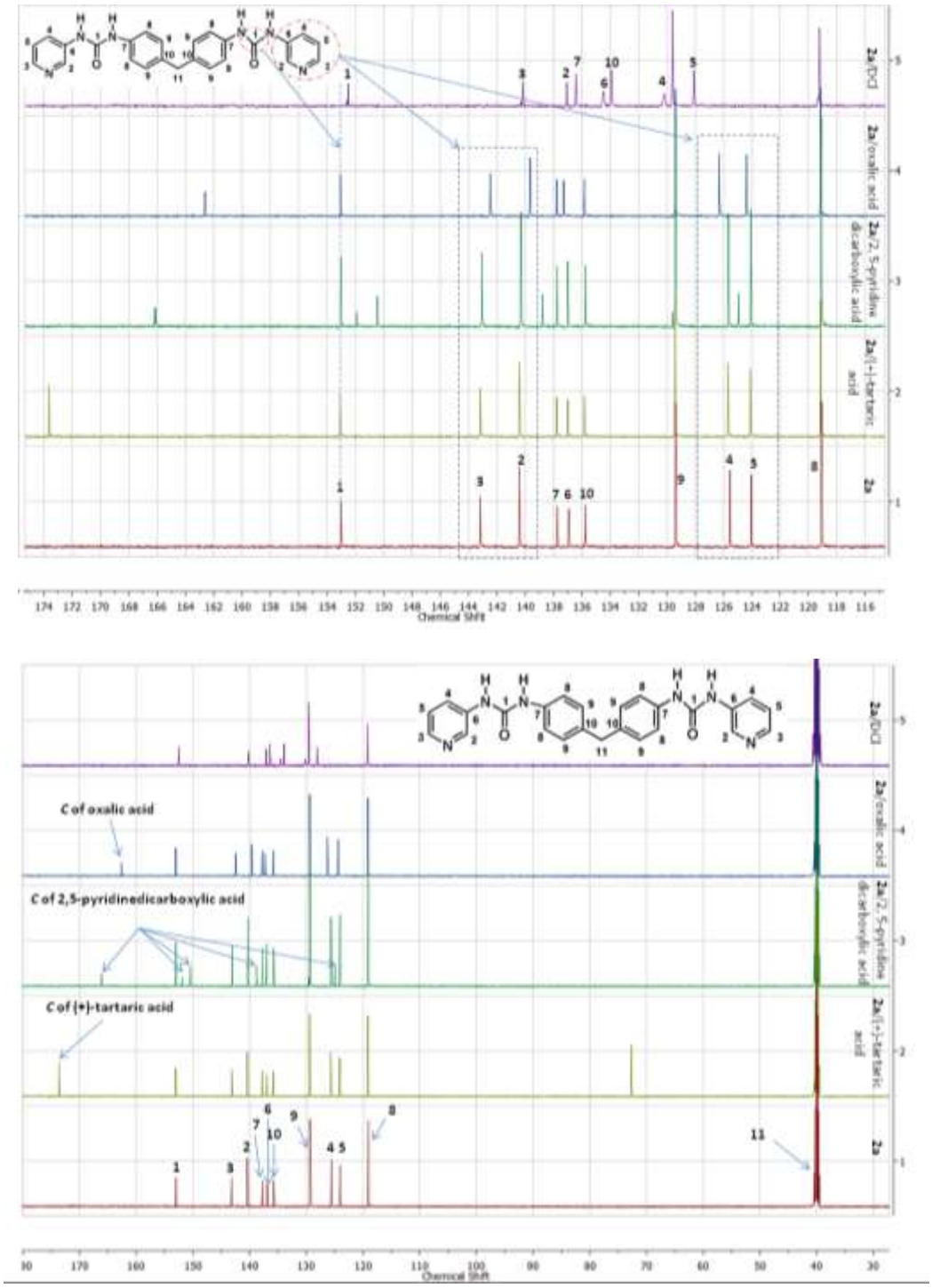


Figure S18 Full and partial ^{13}C NMR spectra of **2a**, **2a**/oxalic acid, **2a**/2, 5-pyridinedicarboxylic acid, **2a**/(+)-tartaric acid and **2a**/DCl in d^6-DMSO (1:1)

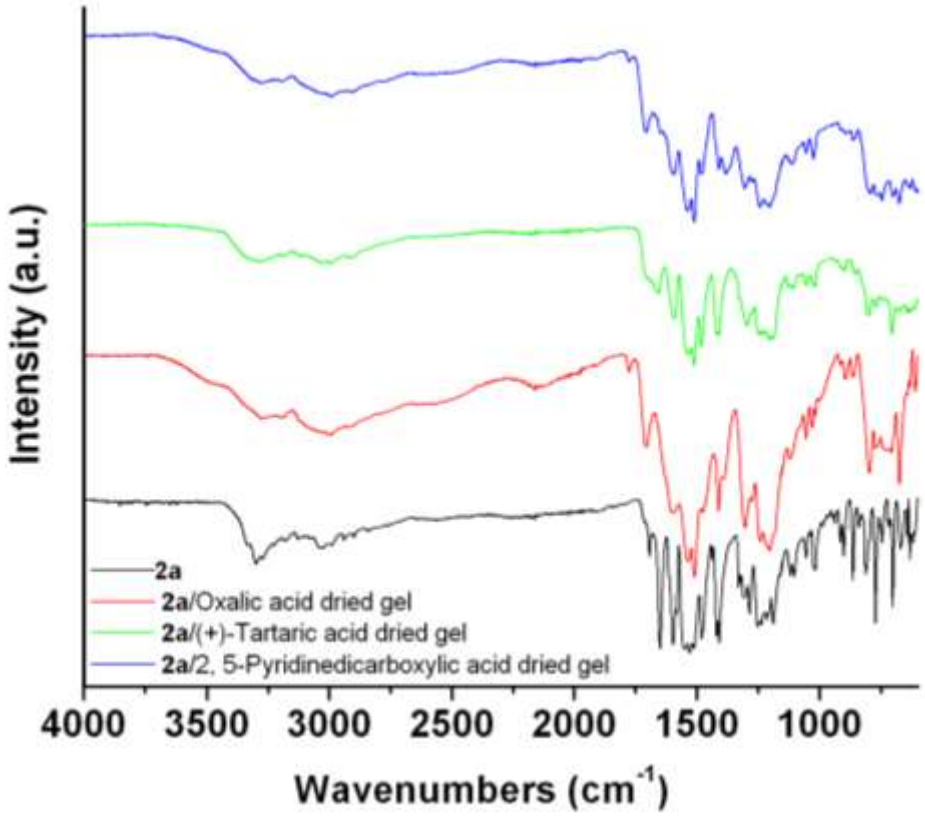
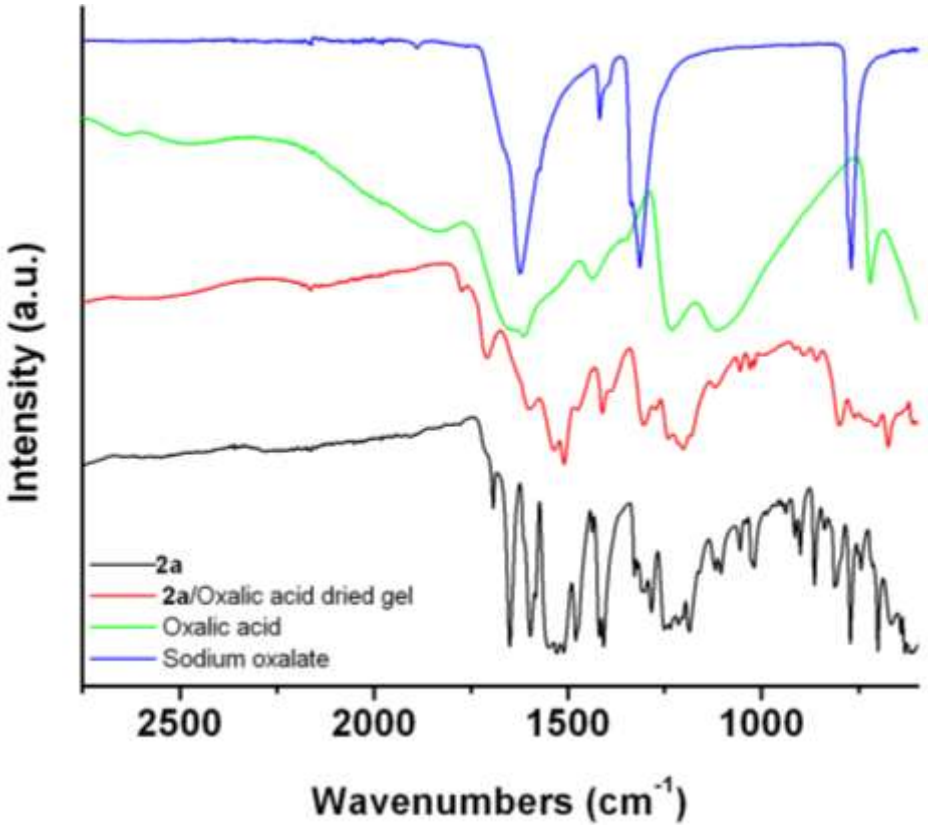
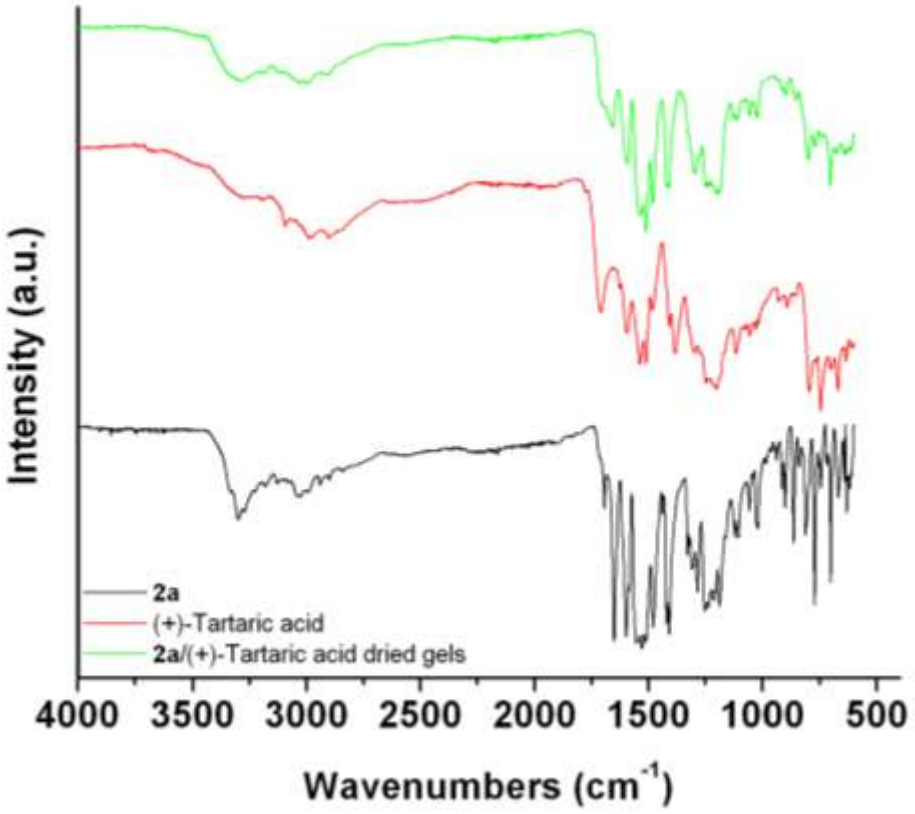


Figure S19 Full IR spectra of **2a** and dried gels of **2a**/oxalic acid, **2a**/(+)-tartaric acid and **2a**/2, 5-pyridinedicarboxylic acid



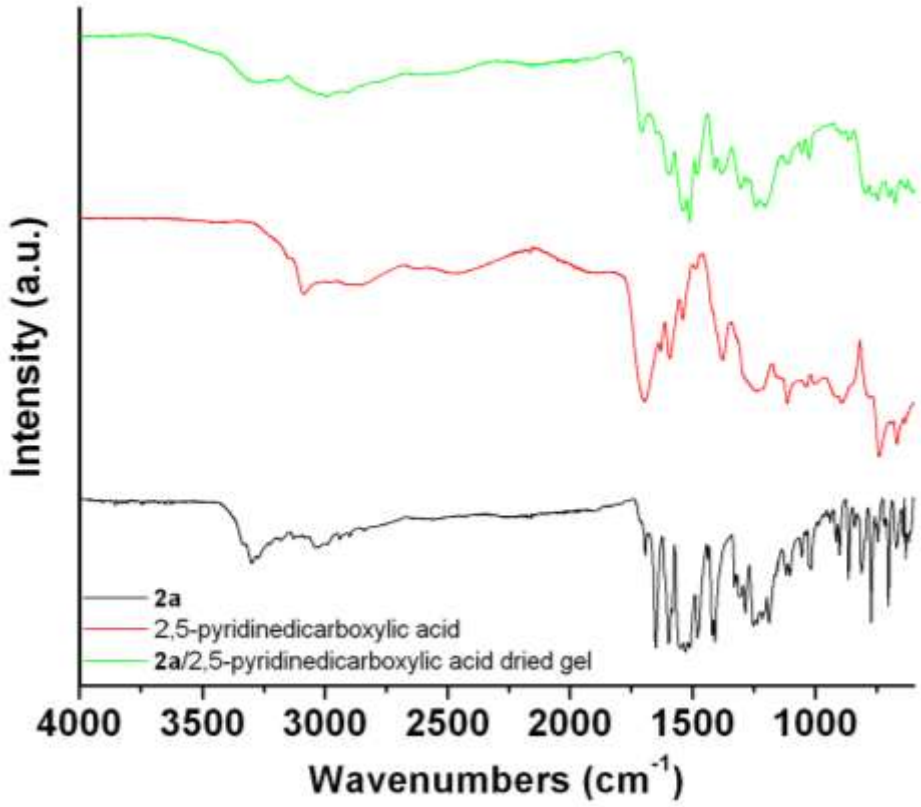
Samples	IR signals (cm^{-1})
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2a/Oxalic acid dried gel	3278.0; 3034.8; 1776; 1709.8; 1599.06; 1535.07; 1509.28; 1472.98; 1401.9; 1303.9; 1269.5; 1239.9; 1200.8; 1119.6; 803.44; 763.33; 706.97; 677.37
Oxalic acid	3416.97; 1611.48; 1436.7; 1235.2; 1104.7; 724.17
Sodium oxalate	2935.1; 1618.04; 1414.1; 1309.9; 769.2

Figure S20 Full IR spectra of oxalic acid, sodium oxalate and **2a**/oxalic acid dried gel



Samples	IR signals (cm^{-1})
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2a/(+)-Tartaric acid dried gel	3288.3; 1701.8; 1652.2; 1591.5; 1533.9; 1509.9; 1476.3; 1432.4; 1294.0; 1198.04; 1112.8; 1111.7; 1054.1; 1018.9; 897.4; 854.2; 799.8; 767.8; 703.9
(+)-Tartaric acid	3091.60; 2987.6; 2898.1; 1706.6; 1626.6; 1591.5; 1533.9; 1509.9; 1476.3; 1409.2; 1380.4; 1297.2; 1198.04; 1114.9; 1054.1; 793.4; 742.4; 695.9; 667.08; 631.9

Figure S21 Full IR spectra of **2a** and (+)-tartaric acid and **2a**/(+)-tartaric acid dried gel



Samples	IR signals (cm^{-1})
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2, 5-Pyridinedicarboxylic acid	3146.6; 3086.2; 1696.6; 1628.6; 1590.8; 1536.5; 1686.6; 1374.9; 1235.9; 1113.5; 1036.5; 1003.3; 891.5; 735.9; 667.9
2a/2, 5-Pyridinedicarboxylic acid gel	3278.0; 1176.6; 1710.2; 1648.3; 1590.8; 1533.5; 1509.3; 1479.1; 1408.1; 1380.9; 1303.9; 1272.1; 1241.9; 1198.1; 1113.5; 1053.1; 1025.9; 745.0; 701.2; 674.0; 633.2

Figure S22 Full IR spectra of **2a** and 2, 5-pyridinedicarboxylic acid and **2a**/2, 5-pyridinedicarboxylic acid dried gel

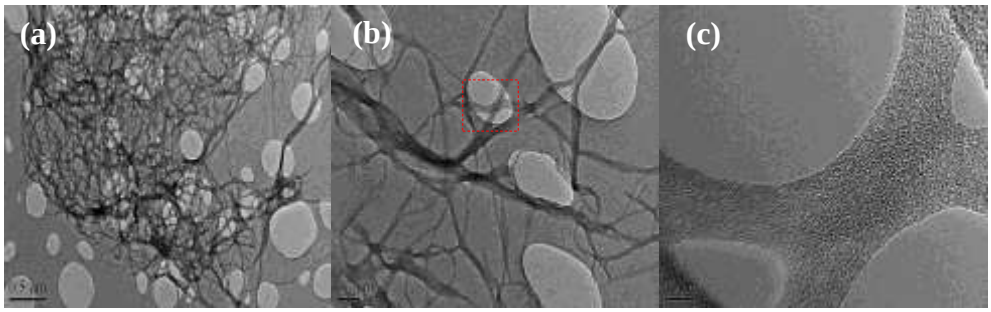


Figure S23 TEM images of the diluted sol of the **2a**·oxalic acid (1:1, 0.05 w/v%) Bar: 0.5 μm, 0.1 μm and 10 nm